Chem Ed

EDITORIALLY SPEAKING

The greatest thing in chemistry is a great chemist. On June 15, 1959, Samuel Colville Lind will be eighty years old. He has spent 54 of those years in chemistry, 29 in universities, 13 in government service, and 12, after retirement, in his present position as consultant at Oak Ridge. The length of his career is unusual in itself, but from the standpoint of chemical education it has a particular interest, since Lind is one of the last of those chemists who, around the beginning of the century, went to Germany for advanced training.

A native of Tennessee, Lind received his bachelor's degree at Washington and Lee University. He started to major in classics, but a university requirement led him to elect the elementary chemistry course in his senior year. Professor James L. Howe, an expert on the platinum metals, was so winning a teacher that Lind determined to make chemistry his career. He returned for an extra year to complete his elementary training in chemistry and then moved to M.I.T. for two years, receiving the B.S. in 1902.

After a year as assistant in analytical chemistry, M.I.T. awarded him a Dalton Traveling Fellowship, for a year of study at Ostwald's laboratory in Leipzig, then the mecca of American physical chemists. Ostwald was relatively inactive in research and, partly by chance, Lind sought a problem from Bodenstein, who set him to studying the thermal reaction between bromine and hydrogen. Bodenstein had previously discovered that the kinetics of the analogous system, hydrogen-iodine, were quite straightforward, conforming to a second-order equation. Lind discovered a quite different relationship in the case of bromine, and the kinetic equation which he obtained remained unexplained for thirteen years. Some fifty years have, however, not altered its validity and the research stands as one of the classics of chemical kinetics. It is almost invariably quoted as an elegant example in textbooks of elementary physical chemistry.

Armed with the Ph.D. for this work, he joined the staff of the University of Michigan. After five years he obtained a leave of absence to study the newer branches of chemistry for a year in Europe. The first part of the year was spent in Marie Curie's laboratory in Paris, where he was introduced to experimental radioactivity. He carried out research on the combination of hydrogen and bromine and on the decomposition of hydrogen bromide under alpha-ray bombardment. He spent the latter part of the year in Vienna at the new Institut fur Radiumforschung where he studied the ozonization of oxygen by alpha rays, measuring for the first time both the amount of chemical change and the ionization produced in the same medium.

In 1913 he joined the Bureau of Mines as the expert on radioactivity to take part in their program for isolating some eight grams of radium from Colorado carnotite. This understaking was sponsored jointly by the Bureau of Mines and the National Radium Institute, which had been formed to obtain radium for experimental therapeutic uses. At the end of the production operations about half a gram of radium was in excess of the amount required by the National Radium Institute, and this was made available to him for experimental work on chemical reactions initiated by radiation. He did the first of this at Golden, Colorado, and continued it after 1920 in Reno, Nevada, and after 1923 when he succeeded R. B. Moore as chief chemist of the Bureau of Mines at Washington, D. C. He left the Bureau of Mines in 1925 to become associate director of the Fixed Nitrogen Laboratory of the Department of Agriculture. Finally, in 1926, he returned to academic life as Director of the School of Chemistry of the University of Minnesota. Nine years later he was made Dean of the Institute of Technology, a position he held until his retirement.

After retiring in 1947 he returned to Tennessee, becoming a technical consultant at Oak Ridge. From 1951 to 1954 he was Acting Director of the Chemistry Division of the Oak Ridge National Laboratory. The half gram of radium which he used at the Bureau of Mines was loaned to him on his departure and was used by him and his students throughout his career.

S. C. Lind's service to chemistry and chemists has been monumental. From 1908 to 1929 he served *Chemical Abstracts* and later was on the editorial board of *JACS* and *Chemical Monographs*. From 1933 to 1951 he was editor of the *Journal of Physical Chemistry*. His authoritative monograph, "The Chemical Effects of Alpha Particles and Electrons," first published in 1928 is currently undergoing its third revision. Among the many honors he has received, the ACS chose him President in 1940 and Priestley medalist in 1952.

Radiation chemists universally regard S. C. Lind as their esteemed dean. His pioneering work on the quantitative measurements of chemical change and ionization is the foundation of the science. It is most fitting that the symposium designed to set forth the present state of knowledge in historical perspective be called the Lind Jubilee Symposium on the Development of Radiation Chemistry.

A ChemEd SYMPOSIUM

Development of Radiation Chemistry

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Early Contributions by S. C. Lind to the Radiation Chemistry of Gases

The title of this report restricts this presentation to the work of Dr. Lind in the field of radiochemistry only. However, it would be a serious omission to fail to mention his earliest and very interesting research which he carried out with Professor Bodenstein in Leipzig in 1905. It certainly is most important on this occasion to cover an individual's Life-Work rather than to stay within the narrow confines of a given field of chemical research.

Furthermore it will not be possible to discuss the researches carried out by Dr. Lind and his collaborators in great enough detail to do justice to this investigator. Hence only certain researches will be mentioned with the hope that the choice made will present a proper picture of Dr. Lind's scientific stature. The first scientific problem studied by Dr. Lind had to do with the rate of formation of hydrogen bromide from its elements.

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Hydrogen Bromide Synthesis

This investigation is his "Inaugural Dissertation der Hohen Philosophischen Fakultät der Universität Leipzig zur Erlangung der philosophischen Doktorwürde, eingereicht von S. C. Lind aus McMinnville, Tennessee." This statement refers to his Ph.D. thesis "Über die Bildung des Bromwasserstoffgases aus den Elementen." In earlier work Professor Bodenstein had demonstrated the existence of simple bimolecular processes in the reaction system hydrogen + iodine → hydrogen iodide. The work of Dr. Lind showed that the reaction between hydrogen and bromine proceeded by a system of complex bimolecular kinetics. The synthesis became a classical example of such complicated reaction mechanisms. This research in itself established Dr. Lind as a thorough and competent investigator. This experimental work was carried out in 1905 (*1*). It is of interest to record the summary of this paper because it shows the careful experimental work, the clear thinking, and the concise mode of expression which are known to be Dr. Lind's basic characteristics. To wit:

(1) In order to find a connection between free energy and reaction velocity of analogous reactions, the rate of the formation of

The American contingent at Ostwald's laboratory in Leipzig (1904–1905). Reading left to right: Colin G. Fink, Samuel C. Lind, W. T. Metcalf, John P. Mitchell, Arthur B. Lamb ( ) Sammet, William C. Bray, Thomas F. Rutter, and William H. Sloan.

The Cover

The papers of the Lind Jubilee Symposium begin in this issue. The cover feature is the focus of this symposium: the contributions of S. C. Lind's half century of scientific work. Seldom does a biography relate so completely the development of a whole field of investigation.

The Editor gratefully acknowledges the generous assistance of Dr. Ellison H. Taylor of the Chemistry Division of the Oak Ridge National Laboratory in the preparation of the biographical material and in obtaining the photographs.

hydrogen bromide from its elements was investigated. A similar study had earlier been made for the formation of hydrogen iodide.

(2) The reaction took place at 200–300°C with a conveniently measurable rate, which was very reproducible and free from disturbing effects, as perhaps due to the walls of the reaction vessel and maybe to traces of foreign gases, etc.

(3) The reaction rate did not correspond to the expected second order. It was much more complex. The formation of the product depended on the first power of the hydrogen concentration, the square root of the bromine concentration and upon another factor, expressing the reduction of the rate of production of hydrogen bromide by this gas itself. Hence, it appears to be a case of negative auto-catalysis.

(4) This retardation is an effect due to the hydrogen bromide produced and is very specific, because other substances such as carbontetrachloride, water, and air are without influence, whereas iodine even surpasses hydrogen bromide in its effect.

(5) The reason for this retardation is not to be found in any chemical factors: A complex like $(HBr)_x$ is not found. Simple physical causes could not be discovered, and only very uncertain suppositions could be offered in explanation.

(6) The temperature coefficient of the reaction is normal, but perhaps a little larger than is usual.

(7) Since a simple rate-expression does not describe the observations, these results are not useful for the purpose stated under paragraph (1) of this summary.

It was not until 1919 that Christiansen (*2*), Herzfeld (*3*), and Polanyi (*4*) invented independently a reaction mechanism which fitted the experimental results embodied in Dr. Lind's Ph.D. thesis. The rate expression is

$$\frac{d(HBr)}{dt} = \frac{k_r(H_2)\cdot(Br_2)^{1/2}}{1 + k_r'(HBr)/(Br_2)}$$

and the reaction steps are (*5*)

$$Br_2 \rightleftharpoons 2Br \qquad (1)$$

$$Br + H_2 \rightarrow HBr + H \qquad (2)$$

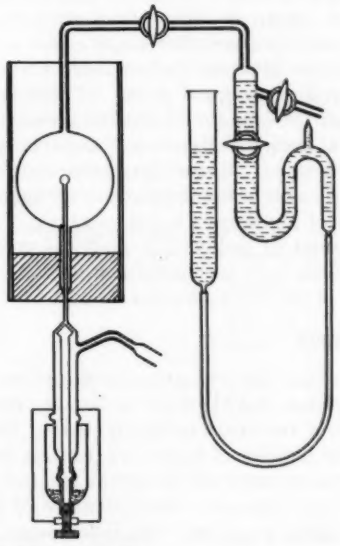
$$H + Br_2 \rightarrow HBr + Br \qquad (3)$$

$$H + HBr \rightarrow H_2 + Br \qquad (4)$$

They yield the rate expression found by Lind. It is of interest to note that the discovery of this atomic-molecular mechanism by the three investigators mentioned represents another case of the simultaneity and originality of human thought which occurs so often in the fields of science and invention (*6*). Few Ph.D. theses cover more important results than did Dr. Lind's work in the late Professor Bodenstein's laboratory.

Hydrogen Bromide Synthesis by Radium-Emanation

At the turn of the century a number of outstanding new scientific phenomena were observed: Roentgen discovered X-rays (1895), Becquerel found that uranium minerals gave off some kind of penetrating radiation (1896), and the Curies discovered the elements polonium and radium (1898). It was quite natural that chemists would consider the use of the powerful rays emanating from these materials as a means of imparting energy to potentially reactive systems. It was also natural that Dr. Lind, of a curious turn of mind, would become interested in this new field of "radiation chemistry." Having studied the kinetics of hydrogen bromide synthesis, he was bound to wonder what chemical effects these new radiations would have on this system (*7*). In a way he noted that the few reactions which had been studied were of a qualitative character and only the relative order of magnitude of these reactions was known. Nor did there exist any definite knowledge of the amount of energy produced in these chemical systems by the radiation traversing it. Nor was it known what relation, if any, existed between this radioactive energy and the chemical energy of the induced reaction. It seemed obvious that the chemical system would have to absorb the incoming energy at least partially in order to react. In the hydrogen bromide system it was found that the liquid phase showed greater reaction than the gas phase and that the effects of alpha, beta, and gamma rays were larger in this order. It seemed also probable that these radioactive effects would show quite specific sensitivity for certain reactions. Such was found to be the case in the hydrogen-bromine reaction which was many orders of magnitude smaller than the reaction between hydrogen and chlorine (*8*) even though the absorption of radiation favored the bromine reaction. Dr. Lind found only very small combination between hydrogen and bromine and very little decomposition of hydrogen bromide by beta and gamma rays. However, alpha rays produced combination at a measurable rate but in no comparison to the reaction produced in hydrogen-chlorine mixtures.



Alpha ray bulb (Ref. (*11*), p. 88.

The method of introducing the reactants and the radium emanation used in these reactions was difficult and time-consuming and was greatly improved by the use of the alpha ray bulb. Rutherford and Royds (*9*) had managed to produce capillary glass tubes with walls so thin that alpha particles could penetrate them. Lind (*10*, *11*) and Duane made an ingeneous modification in the laboratory of Mme. Curie by constructing a small thin-walled bulb which was placed in the center of the reaction vessel (see figure). There are several advantages in the use of this bulb when filled with radon. The latter is separated from the reaction system. The alpha ray bulb permits the use of a flow system by which large quantities of reactants are exposed to the radiation, and gaseous products are continuously removed, thus reducing the reverse reaction to a minimum. And,

furthermore, a fuller utilization of the entire alpha radiation is possible by employing a vessel of large enough diameter so as to prevent the alpha rays which leave the central bulb from reaching the walls of the reaction vessel (*11*).

The Role Played by Ions

At this time (1912) Lind (*12*) considered the theoretical aspects of alpha ray reactions. He proposed that, in all gas reactions and also those where both gases and liquids were present, the chemical effects produced by alpha particles are determined by the number of ions formed in the reaction mixture. Hence it is necessary to consider all those variables such as pressure, change of pressure, mean length of path, or composition, which in any way may influence the formation and the concentration of any ionic species conceivably formed in the reaction system. It was therefore necessary to calculate the average path of alpha particles in various shaped vessels so as to be able to estimate the ionization of a gas by the radon and its decomposition products. The natural factor to be determined for any radon induced reaction would hence be the ratio of molecules formed or decomposed as related to the number of ions produced from the radioactive elements in the same length of time. In a general way it appeared in several cases that there exists a one-to-one correspondence between the number of ion pairs and the number of reacting molecules. This relation would indicate that the ions constituted a necessary precursor for chemical action. Hence it should be possible to predict the extent of reaction produced in a given system by the amount of the radioactive agents present. The action of alpha rays is not catalytic. It depends on the amount of radioactive material present. The action of beta rays is commensurate with the small proportion of relative ionization produced by these rays.

The M/N Ratio

The idea that the ionization produced by the alpha rays from radon should be the causative agent in these radiochemical reactions naturally led to the attempt to relate the number of molecules reacting to the number of ion pairs produced during the reaction time. In 1911 Lind (*10*) measured the quantity of ozone produced by alpha particles from radon when acting on gaseous oxygen and compared this amount with the ionization produced. He used an alpha-ray bulb twelve centimeters in diameter so that the range of the alpha rays was fully utilized. The ozone produced was determined by absorption in neutral potassium iodide solution. It appeared that the number of molecules of ozone formed and the total number of ion-pairs produced during the duration of the experiment were about in the ratio $M/N \sim 2$. In this case deozonization also takes place and must be avoided. It can be done by removing the ozone formed by alpha radiation on a surface of mercury.

At this stage of development of radiochemical reactions it was necessary to determine the average path of an alpha particle traversing a gas space in the case that the radon was distributed throughout the gas volume. This geometric problem was solved in several ways by Dr. Lind and others (*13*). Naturally many more reactions were studied and in 1921 Dr. Lind summarized the field in his well-known ACS monograph on "The Chemical Effects of Alpha Particles and Electrons." A revised edition appeared in 1928 (*14*). These monographs contain very complete lists of reactions studied by various investigators, and the corresponding M/N ratios are given and thoroughly discussed. A natural development was the study of the kinetics of these radiation-induced reactions, for example, the formation of liquid water from its elements (*14*). The importance of the ion pair in these reactions is given in Dr. Lind's own words (*11*):

> The M/N ratio varies from 1 to 20 in most reactions. Values above unity are interpreted as the result of ion clustering, support of which is to be seen in the direct addition of lower hydrocarbons to form higher ones and in the frequency with which liquid and solid products result from the primary step of ionization, especially in the reactions with the higher M/N ratios. The latter ratios above unity are not to be interpreted as due to a chain mechanism, because of the complete absence of chain characteristics. These features do exhibit themselves in the combination of hydrogen and chlorine gases, which is a true chain reaction, where M/N however lies not in the region 1–20 but from 1000 to 500,000 molecules of hydrogen chloride gas per ion pair.
>
> The second evidence is the fact that whether the ions be produced by alpha particles, beta particles, recoil atoms, or electrons, the M/N ratio is the same for a given reaction.
>
> The fact that when the ratio of two reactants is varied in either direction from the equivalence mixture the velocity change quantitatively as required by the change in the specific ionization while the M/N ratio remains constant, is proof of the strongest character that ionization is the primary step. Finally if an inert gas be added in different reactions, the velocity is increased exactly in proportion to the additional number of ions thus produced in the system, while the M/N ratio again remains constant, N being the total number of ion-pairs including those of the inert gas.

From the M/N ratio and the heat of the reaction it can be calculated that the utilization of the energy residing in the alpha particle is very low: Decomposition of water (6.4%), hydrogen chloride (1.8%), hydrogen sulfide (6.7%), hydrogen bromide (2.2%), and ammonia (1.2%). It is also true of photochemical actions where the absorbed radiation must bring the reacting species to a much higher energy state, a process which requires more energy than results from the subsequent chemical reaction.

Catalytic Effect of Inert Ions

The rates of a number of reactions, as for example the polymerization of acetylene to a solid polymer are enhanced by the admixture of an inert gas. In this case nitrogen gas will form ions like acetylene and both types of molecules will contribute to the polymerization. In general it is found that

$$\frac{\text{Velocity of } (C_2H_2 + N_2)}{\text{Velocity of } (C_2H_2)} = \frac{\text{Total Ionization } (C_2H_2 + N_2)}{\text{Partial Ionization } (C_2H_2)}$$

The simplest idea to account for this effect is to suppose that inert ions can serve as clustering centers as well as the reacting species. In the case of acetylene polymerization

$$C_2H_2^+ + 19C_2H_2 \rightarrow (C_2H_2)_{20}^+ + e^- \rightarrow (C_2H_2)_{20}$$

or

$$N_2^+ + 20C_2H_2 \rightarrow [(C_2H_2)_{20} \cdot N_2] + e^- \rightarrow (C_2H_2)_{20} + N_2$$

Reactions in Electrical Discharge

It had been known since the invention of the Geissler tubes that chemical effects could be produced in electric

discharges of all description. Even before this period open discharges in air were known to cause the production of nitrogen oxides and the formation of ozone. In the period from 1876 to date M. Berthelot and many other investigators studied the chemical effects in all sorts of electric discharges (*11*). Naturally Dr. Lind wondered what connection if any there existed between the radiochemical alpha ray reactions, discussed above and the same reactions produced in some form of electrical discharge. Under a Grant from the American Petroleum Institute (1926–31) Lind, Glockler, and Schultze studied the effects of various forms of electric discharge (ozonizer, corona, and semi-corona) on the gaseous hydrocarbons methane, ethane, propane, butane, ethylene, and acetylene. The general field of research of these effects was covered in a monograph on this subject (*14*). Alpha ray studies on these gases (*11*) had already established the chief characteristics of these reactions, namely that the saturated hydrocarbons condense with evolution of hydrogen and methane to form higher members even up to liquids and solid products. The yield is constant, two molecules reacting per ion pair, for methane, ethane propane, and butane; the gas pressure remains nearly constant. The unsaturates condense with a much smaller gas evolution but with a larger yield per ion pair showing that gas evolution is by no means a criterion of the rate or extent of reaction.

The objective of the experiments with electric discharge in hydrocarbon vapors was largely directed toward the question as to whether the same characteristics would manifest themselves as in the alpha ray reactions. If so, then the conclusion might fairly be drawn that the same relations exist between the chemical reaction and the gaseous ionization both qualitatively and quantitatively. Since ionization in an ozonizer, for example, will be difficult to measure or to calculate it was impossible to determine the ion yield. Hence the importance of the yield in alpha ray reactions can be appreciated.

In the case of ethane, a liquid product was readily obtained. The fraction of hydrogen of the total H_2-CH_4 mixture obtained was 0.75 in the silent discharge and 0.83 in the alpha ray case. The disappearance of the initial ethane to the hydrogen produced was 1.4 and 1.3, respectively, in the same reactions. The composition of the liquid product was found to be $C_nH_{1.80n}$ and $C_nH_{1.85n}$, respectively. It was of interest to analyze the products of the electrical discharges on simple hydrocarbons, and Lind and Glockler (*15*) arranged a bank of twelve ozonizers in parallel and prepared 833 grams of liquid hydrocarbons from 5420 grams of butane gas. Fractional distillation showed that the liquid product was a very complex mixture of hydrocarbons. It was of interest to discover that octanes were relatively more abundant than other species of molecules. This finding is expected on the ion-cluster theory:

$$C_4H_{10} \rightarrow C_4H_{10}^+ + e^-$$

$$C_4H_{10} + C_4H_{10}^+ \rightarrow (C_4H_{10}\cdot C_4H_{10})^+$$

$$(C_4H_{10}\cdot C_4H_{10})^+ + e^- \rightarrow C_8H_{18} + H_2$$

$$2C_4H_{10} \rightarrow C_8H_{18} + H_2$$

It seems quite clear that there is some analogy between alpha ray activated and electric discharge reactions at least in a qualitative way. While the number of ions produced and the number of molecules reacting can be determined in an alpha ray reaction, it does not seem to be a simple matter to obtain similar information for the various electrical discharges. Hence it is quite natural that attempts have been made to discuss these two types of reaction on the basis of atomic and radical processes.

Atom and Radical Mechanisms

These processes have naturally been suggested for reactions where no ions or electrical charges are present. To be sure the greatest number of reaction mechanisms are really only reasonable guesses and no direct evidence is available except that the end results could only be attained if certain species of atoms and radicals were present. It is quite natural by the law of parsimony to choose the simplest reaction path consistent with the products. As far as alpha ray and electric discharge reactions are concerned, it is clear that radiation is produced from molecules and radicals and atoms, the spectra of which are well known. Hence these species must be present and must be considered as possible reaction intermediates. Only one case can be considered here. It is the famous hydrogen-bromide synthesis which was discussed at the beginning. This reaction was studied by Livingston (*16*), Lind and Livingston (*17*) and by Eyring, Hirschfelder, and Taylor (*18*). An interesting situation arises since it is possible to account for the alpha ray induced reaction also by an atomic mechanism as shown in the table.

Hydrogen Bromide Synthesis[a]
(Molecules HBr appearing per ion pair)

Expt. No.	Experimental value	Ion cluster theory Lind & Livingston	Atomic mechanism Eyring *et al.*
1	0.24	0.27	0.24
3	0.58	0.51	0.48
5	1.90	1.81	1.79
7	2.67	2.16	2.27
..	..	..	..
..	..	..	..

[a] Reference (*15*), p. 442.

The same set of experimental data can be accounted for by two different mechanisms. The difficulty lies in the great complexity of reaction possibilities when activation occurs by either alpha particles from radon or in electrical discharge. As often happens, both theories may be applicable, and ion-clusters, radicals, and atoms will contribute to the mechanism of reaction. These respective reaction paths will very likely be of relatively different quantitative importance in different reactions.

When the evidence for an ion-cluster reaction mechanism as given by Dr. Lind and cited above is considered, it surely may be said that many reactions will follow this path, if not exclusively then surely to a large proportion of the various possible modes of interaction between the molecular species involved.

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Development of The Radiation Chemistry of Aqueous Solutions

Aqueous radiation chemistry began when dissolved radium salts were found to decompose water. Later it was found that chemical reactions took place in water and aqueous solutions irradiated only by β- and γ-rays of radium. From these modest beginnings, the current prominence of this branch of chemistry has gradually developed. Three periods are: 1900–25, 1925–40, and 1940 to the present. Except for some basic observations little progress was made in the first quarter century. Consequently we shall deal only briefly with this era. But because many basic principles were established in the sometimes overlooked second era, we shall discuss this period at some length; and then because we are familiar with prodigious post-war developments, we shall treat these only lightly.

Early Period (1900–1925)

Radium salts and radon decompose aqueous solutions liberating hydrogen, oxygen, and hydrogen peroxide. These effects were described by Geisel (*1*) in 1902 and were later studied by Cameron and Ramsey (*2*), Debierne (*3*), Kernbaum (*4*), Usher (*5*), and Duane and Scheuer (*6*). The decomposition of water into hydrogen and oxygen was regarded as an electrolysis because it was known that an ionized gas conducts an electric current and that an electric current passing through a solution liberates hydrogen and oxygen at the electrodes. These radiation effects are due principally to the release of α-particles from the radium. However, β-ray and γ-ray effects on aqueous solutions were also studied although to a lesser extent.

The penetrating β-rays and γ-rays of radium decomposed water and promoted reactions in aqueous solutions. Through a 0.5-mm glass tube, these rays caused about 1% as much evolution of gas as did the dissolved radium salt itself (*4*). The gas is almost exclusively hydrogen while the hydrogen peroxide remains in the solution. Thus the water decomposition reaction is:

$$2H_2O \rightarrow H_2 + H_2O_2$$

Besides water decomposition, the radiations from radium salts reduced ferric sulfate, and they liberated halogens from alkali and alkaline earth iodides and bromides (*7*). These experiments were carried out with 80 to 200 mg radium and were scarcely more than qualitative in nature because of the small effects produced. But these researches showed that chemical reactions took place and thus they set the stage for the next major development in radiation chemistry, the use of the X-ray tube.

Although Röntgen discovered X-rays in 1895, chemical applications of X-rays were not made for almost a quarter of a century. Indeed, even after the discovery of the modern hot filament-anode tube by Coolidge (*8*) in 1912, the principal applications of this new powerful tube were in industrial and therapeutic radiology, and in physical research. Not until the mid-twenties were X-rays applied to chemical studies. The principal incentive came, not through chemical research, but through studies on the biological effects of X-rays.

During this early period water decomposition by α-rays was established and a good idea of the radiation yields was obtained. Chemical reactions in aqueous

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solutions were also qualitatively explored but chemical research was retarded because of inadequate irradiation sources.

Intermediate Period (1925–1940)

The principal drawback to progress on the radiation chemistry of liquids and the reason for its great development in this stage are set forth by Lind in 1928 as follows (*9*):

> Owing to their great penetrating power it is difficult to utilize γ-rays efficiently in the study of radiochemical effects. The subject seems to have great importance, however, since it is the γ-rays which are utilized therapeutically, but whether or not the effect is produced through the intermediation or chemical action remains as yet wholly unknown.

And while these remarks were being written, Fricke, a biophysicist, and his collaborators were studying the chemical effects of X-rays in aqueous solutions in order to understand the underlying mechanisms of radiobiology.

Fricke Dosimeter

During this period more powerful and reliable X-ray tubes were used, a chemical dosimeter was developed, and the radiation yields for a number of chemical systems were established. On the theoretical side, in addition to the principle of the indirect effect, chemical action was interpreted by Fricke's activated water hypothesis and the yields of these activated water molecules were estimated.

By 1930 powerful X-ray tubes operating at one million volts and higher had been developed. The X-ray output of these tubes provided radiation sources equivalent to thousands of curies of radium. Thus radiation research on a scale undreamed of before 1925 was possible. While these tubes were not used for chemical studies, specially developed five-inch tubes with a water-cooled tungsten anode operating at 100 kv and 5 to 50 ma were in use at the Long Island Biological Laboratory from 1929 to 1938. Tubes with similar characteristics were in use in other laboratories.

Studies on the oxidation of ferrous sulfate by X-rays were most fruitful. Out of these studies emerged the "Fricke dosimeter," the principle of "indirect action" and the effect of oxygen. Let us see how studies on this remarkable system developed.

Biologists knew that protein activity was destroyed by irradiation in aqueous solutions. Hemoglobin, a crystallizable protein containing an iron atom, in the ferrous oxidation state was changed on irradiation in aqueous solution to methemoglobin containing ferric iron (*10*). But since there were only four ferrous atoms per protein molecule of 68,000 molecular weight, the action of the rays was, indeed, highly selective. Furthermore the methemoglobin was formed at a rate nearly independent of its concentration, a fact that indicated a primary action on the water rather than on the hemoglobin. Apparently the water was of prime importance but a simpler system than hemoglobin was needed. Because there was a striking change in the oxidation state of the iron, what system could be more natural than a study of the ferrous oxidation? A more complete knowledge of this system, it was reasoned, might be useful in explaining the chemical effects occurring in irradiated hemoglobin.

As we now know, the ferrous sulfate reaction possesses most of the characteristics of the ideal dosimeter. Although it was developed by 1930, its current importance in radiation chemistry is attested by its widespread usage and study. Hundreds of papers have appeared on this single system. Within wide limits, ferrous sulfate oxidation is independent of ferrous ion and oxygen concentrations, of dosage rate, and of temperature.

In 1935, Reginald Harris foresaw the value of this dosimeter to physicians when he wrote (*11*):

> A small amount of a chemical solution which has been treated by the physician's own X-ray machine could be sent to a central bureau where chemical analysis would tell the dose of X-rays to which the chemical had been subjected. Such a method would be very inexpensive and should largely eliminate mistakes sometimes made in measurement of doses of X-rays used in medical treatment.

While practicing radiologists may not use ferrous sulfate dosimeters, they are used on a wide scale by many research workers engaged in radiation research.

Studies on the ferrous sulfate system confirmed the indirect action effect, and revealed the importance of oxygen, *p*H, and impurities on X-ray initiated reactions. The oxidation yield is independent of ferrous ion concentration from 10^{-5} to 10^{-2} *M* ferrous sulfate in 0.8 *N* sulfuric acid (*12*, *13*). This fact supports the conclusion that the oxidation is due to a primary activation of water.

Since the ferrous sulfate dosimeter was developed for X-ray therapy, it was essential that the chemical dosimeter and the standard air ionization chambers respond alike to X-rays of different wavelengths. Fricke estimated that the necessary equivalence between air and the dosimeter solution is achieved when 0.8 *N* sulfuric acid is used. Agreement to within 1% between air and ferrous sulfate dosimeters was found for the wavelength range of 0.2 to 0.75 Å after corrections were made for the decrease in intensity of the radiations as they passed through the media of the two dosimeters. The first part of the dosage curve in Figure 1 is typical of the linear response of the Fricke dosimeter to ionizing radiations. The chemical effect is strictly proportional to the dosage as long as ferrous ion and oxygen remain in the solutions. Oxygen from dissolved air was shown to participate in the

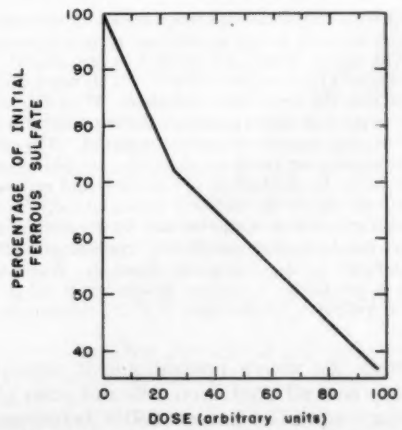

Figure 1. Action of X-rays on ferrous sulfate in 0.8 *N* sulfuric acid (12).

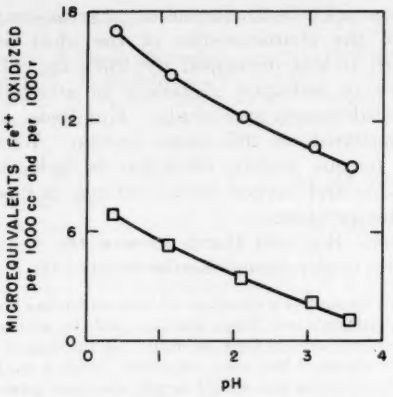

Figure 2. The oxidation of ferrous sulfate in sulfuric acid as a function of pH of the irradiated solution (13).

□ air-free ○ aerated

oxidation and the dosage curve below the "break" in the curve of Figure 1 is typical of the air-free reaction. And since the break is very sharp, oxygen must be effective down to very low concentrations. A *p*H dependent reaction;

$$Fe^{+2} + H^+ + {}^1/_4O_2 \rightarrow Fe^{+3} + {}^1/_2H_2O$$

and a *p*H independent reaction;

$$Fe^{+2} + {}^1/_4O_2 + {}^1/_2H_2O = Fe^{+3} + OH^-$$

were postulated (*13*). The *p*H effect on the yield is shown in Figure 2. Besides *p*H and oxygen effects, impurities must be rigidly controlled in all ferrous sulfate dosimetry and particularly in reactions studied at low concentrations. Much effort was expended on water purification, the perennial problem facing the radiation chemist.

Water Purification and Stability

Traces of impurities radically altered yields in aqueous inorganic systems. Even the relatively inert fatty acids increased the reduction of potassium chromate by more than 100% (*14*). Triply distilled water is traditional since Kailan, in 1911, (*15*) used a triple distillation for water in his radiolysis experiments with γ-rays and β-rays. The L. I. Biological Laboratory's process is described as follows (*16*):

> Water from a Barnstead still was refluxed for extended periods successively in alkali permanganate and in acid dichromate mixtures. The vapor mixed with washed oxygen was then passed through a quartz tube heated to 900°C. This was condensed and redistilled into the evacuation chamber. With this method of purification the organic impurities in the water are effectively decreased but they are not completely removed. The presence of organic impurities can be shown since they are decomposed by irradiation, with the production of hydrogen and carbon dioxide. In Figure 3 are shown the results of such a test on (*a*) water from a Barnstead still and (*b*) water purified by the method described. The water can be further purified by irradiating it after it has been transferred to the evacuation chamber. Water thus purified gave on irradiation no carbon dioxide but it did give a small amount of hydrogen, of the order of 1 or 2 micromoles per liter (Fig. 3*c*).

Even with the above precautions, it was standard practice to heat all irradiation cells and other glassware contacting the purified water to 550°C before use.

The problem of water purity is of greatest importance in studies on the stability of irradiated air-free water. Figure 3 shows that pure water irradiated by X-rays gives no continuous decomposition since the dosage curves rapidly approach zero slope; but the experimental conditions must be closely defined. In the experiments of Figure 3, completely filled and sealed irradiation cells were used and no appreciable hydrogen or oxygen appeared (*11*, *17*). In experiments containing a large gas phase, no peroxide was found in the liquid phase (*18*) although hydrogen was found in the gas phase (*19*). On the other hand, α-rays decomposed water into hydrogen, hydrogen peroxide, and oxygen (*1–6*, *19*, *20*) and the experimental conditions were not particularly critical.

Supporting the idea that impurities affected water stability was the finding that the iodide or bromide ion catalytically decomposed irradiated water (*21*). Equimolar amounts of hydrogen and hydrogen peroxide were formed in yields independent of concentration between 10^{-5} and 10^{-3} molar potassium iodide. In neutral and alkaline solutions, the hydrogen yield was unchanged but the hydrogen peroxide was replaced by an equivalent amount of oxygen. At low iodide concentrations, the amount of water decomposed was many times the iodide ion concentration.

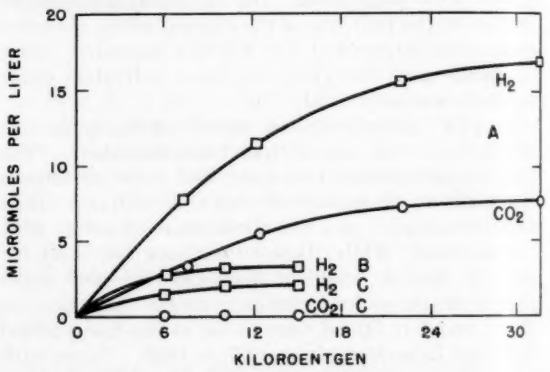

Figure 3. Decomposition of organic impurities in water by irradiation with X-rays (16). *A*, water from Barnstead still; *B*, chemically purified water; *C*, irradiated water.

Studies of Chemical Reactions

The potentialities of ionizing radiations for chemical research developed during this second stage. Photochemical studies usually paralleled radiochemical studies but Kailan found that his radiochemical effects were several hundred fold feebler than his photochemical effects. However as more powerful ionizing sources became available, the low X-ray absorption coefficients of water proved advantageous over the high optical absorption coefficients of many molecules and ions. Except for the "track-effect" a more homogeneous distribution of the reactive species resulted from X-ray activation than from photochemical activation.

Inorganic reactions studied included the formation and decomposition of hydrogen peroxide (*18*, *22*), decomposition of hydrogen bromide and iodide (*19*, *21*, *26*), the reduction of permanganate (*23*), dichromate (*14*), ceric sulfate (*23*), potassium iodate (*23*), and nitrate (*24*), and the oxidation of ferrous sulfate (*10*, *12*, *13*), nitrite (*25*), selenite (*21*), arsenite (*21*),

ferrocyanide (*21*) and the mercuric chloride oxalate complex (*27*), In addition studies were made on a group of relatively simple organic compounds. Table I contains the yields of some of these reactions. These studies added materially to the knowledge of the chemistry of the individual reactions and confirmed the conclusions drawn from the study of the ferrous sulfate oxidation. Besides, the versatility of the rays in promoting both oxidation and reduction reactions was shown.

Table I. X-ray Yields in Aqueous Solutions, (1925–1940)

Solute	*p*H	Product	μN/l 1000 r	*G*	Ref.
$FeSO_4$	0.5	Fe^{+3}	17.4	16.4	(*14*)
$KCrO_4$	0.5	Cr^{+3}	3.31	3.12	(*14*)
$Fe(CN)_6^{-4}$	2–11	$Fe(CN)_6^{-3}$	1.1	1.20	(*21*)
	2–11	H_2	0.55	0.60	(*21*)
AsO_3^{-3}	2–11	H_2	0.55	0.60	(*21*)
SeO_3^{-2}	2–11	H_2	0.55	0.60	(*21*)
NO_2^-	2–11	H_2	0.55	0.60	(*25*)
O_2	3	H_2O_2	2.2	2.4	(*22*)
	12	H_2O_2	1.1	1.20	(*22*)
I^-, Br^-	3	H_2O_2	0.55	0.60	(*21*)
		H_2	0.55	0.60	(*21*)
Ce^{+4}	1	Ce^{+3}	2.0[a]	6.2	(*23*)
MnO_4^-	1 *N*	Mn^{+2}	3.7[a]	11.6	(*23*)
IO_3^-		IO^-	0.6[a]	1.9	(*23*)
$HgCl_2C_2O_4^{-2}$		HgCl, CO_2	6×10^{8a}	1.7×10^8	(*27*)
CO	3.5	—CO	3.9	4.3	(*16*)
		CO_2	2.45	2.7	(*16*)
		H_2	1.0	1.1	(*16*)
		HCHO	0.3	0.33	(*16*)
HCOOH, 10^{-3} *M*	3.0	H_2	3.2	3.5	(*16*)
		CO_2	3.2	3.5	(*16*)
CH_3COOH 10^{-2} *M*	3.0	H_2	2.5	2.7	(*16*)
		CO_2	0.0	0.0	(*16*)
CH_3OH, 10^{-2} *M*	1.0	H_2	4.0	3.8	(*16*)
	6	H_2	2.0	2.2	(*16*)

[a] Equivalents/ion pair.

Unlike most of the reactions studied, dilute hydrogen peroxide solutions decomposed with yields dependent on concentration, on X-ray intensity, and on temperature. This behavior paralleled the photochemical behavior of this system and it was correctly concluded that a chain reaction developed. Another less studied chain reaction was the decomposition of mercuric chloride oxalate.

Aqueous organic solutions, as expected, in contrast to the simple inorganic ion ones were complex. Hydrogen appeared in all irradiations and carbon dioxide was rather common too (*16*). As with inorganic ions, the radiation yields were independent of intensity and of solute concentration but were markedly affected by *p*H and oxygen. In air-free solutions, hydrogen peroxide was normally not a reaction product. Highly specific reactions occurred and in general the organic molecule underwent both oxidation and reduction reactions. Dissolved carbon monoxide, as an example, was reduced to formaldehyde and it was also oxidized to carbon dioxide and formic acid.

Interpretation

While the activated water hypothesis to be discussed shortly dominated the interpretation of radiation reactions during this period, free radical mechanisms were also conceived. Perhaps the earliest clear ideas were expressed by Risse (*28*) in his explanation of the ferrous sulfate oxidation. He was familiar with the indirect action behavior of water and also with the result that the ferric ion yield was lowered by 50% in the absence of oxygen. He assumed

$$2H_2O \rightarrow 2H + 2OH$$
$$OH + OH \rightarrow H_2O_2$$
$$2H \rightarrow H_2$$

Hydrogen peroxide then oxidized the ferrous sulfate. With oxygen present, twice as much peroxide formed because of the reaction

$$2H + O_2 \rightarrow H_2O_2$$

The activated water hypothesis of Fricke went far in explaining the qualitative and quantitative data of this period (*29*). Two activated water molecules, designated $(H_2O)'_{act.}$ and $(H_2O)''_{act.}$ were proposed. With X-rays of $E_{eff.} = 35$ kv. $(H_2O)'_{act.}$ produced hydrogen with a field of 0.55 μmoles/1000 r · 1000 cc. ($G = 0.60$) and the reaction was written as:

$$(H_2O)'_{act.} + H_2O \rightarrow H_2 + H_2O_2$$

$(H_2O)''_{act.}$ was produced with a yield of 2.2 μmoles/1000 r · 1000 cc ($G = 2.40$) and this molecule specifically activated oxygen leading to the oxidation of four equivalents of ferrous sulfate. Thus we have 8.8 μN Fe^{+2}/1000 r · 1000 cc as the contribution of $(H_2O)''_{act.}$ to the oxidation of ferrous ion in aerated solution. See the nearly constant difference between the aerated and air-free curves of Figure 2. This difference is independent of *p*H, but since the ferric ion yield is *p*H dependent it had to be assumed that the yield of $(H_2O)'_{act.}$ depends on *p*H. (We now know that the *p*H dependence of the air free curve of Figure 2 is due, in part, to ferrous oxidation by hydrogen atoms.) The action of this activated water molecule is more clearly seen if we write the free radical dissociation reaction:

$$(H_2O)''_{act.} \longrightarrow H + OH$$

With oxygen present, our four ferrous equivalents are derived from the hydroxyl and hydroperoxy radicals by the mechanism outlined below.

A comparison of X-ray results was made with photochemical activation of water with light in the first absorption band of water (*29*, *30*). When irradiated by light of $\lambda < 2000$ Å, ferrous sulfate, formic acid, and methyl alcohol solutions were oxidized while nitrite, selenite, arsenite, ferrocyanide, and oxygen solutions remained unchanged (*30*). In this work, water activation occurs in its first absorption band at 1760 Å. It was proposed that $(H_2O)''_{act.}$ was formed by photoactivation of the water molecule in this band. It was hoped that the experiments could be extended to the second absorption band at 1360 Å where it was thought $(H_2O)'_{act.}$ would form. Unfortunately such experiments were not performed and so the fallacy of attributing $(H_2O)'_{act.}$ to 1360 Å absorption was not discovered. We now associate $(H_2O)'_{act.}$ with our "molecular" hydrogen and hydrogen peroxide and do not expect a similar result with any H + OH dissociative process giving an homogenous distribution of radicals.

Water dissociation was considered and abandoned by Fricke. In his words we have:

> We expected, when we started our work on this subject, that X-rays would produce a dissociation of the water molecules, but the finding that water is not decomposed by X-rays, as well as

the closer study of the chemical properties of the X-ray activated water molecule, leave doubt as to the truth of this. If the X-rays did produce dissociation, then the length of life of the activated water molecule, as estimated above, would be the time for recombination of the dissociated parts to take place, and should therefore depend on the X-ray intensity.

It was only in a later period, when high electron beam currents were available that these intensity effects appeared.

Present Period (1940–)

Radiation chemistry emerges as the term denoting this branch of chemistry and the term "radiochemistry" is abandoned, at least by chemists. In the early work, chemical effects were brought about by radioactive elements and we had radiochemistry. In the second stage, X-rays were used and we spoke of "chemical effects of X-rays" or "photochemistry of X-rays." Sometime in the early forties these terms were changed to radiation chemistry. By 1947, the new name was firmly entrenched and used repeatedly in what Lind (*31*) called, "The first symposium on radiation chemistry," a symposium held at the University of Notre Dame in 1948.

After World War II, favorable conditions existed for rapid advances in radiation chemistry. The free radical theory of water radiolysis had been formulated, the mechanism of water decomposition was understood, abundant and powerful radiation sources were available and above all, dozens of laboratories were undertaking radiation research. Progress came rapidly and in this review we shall consider briefly only the major developments.

We have seen how Risse, Fricke, and others considered the hydroxyl and hydrogen radicals as possible intermediates in their studies. It remained, however, for Weiss (*32*) in 1944 to publish the first clear explanation of a wide variety of aqueous radiation reactions. Water decomposed into hydrogen and hydroxyl free radicals according to the reaction:

$$H_2O \rightarrow H + OH$$

Oxidation reactions are promoted by the hydroxyl radical as shown by the oxidation of ferrous ion:

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

Reduction is effected by the hydrogen atom:

$$Ce^{+4} + H \rightarrow Ce^{+3} + H^+$$

Dissolved oxygen promoted further oxidation by the reactions:

$$H + O_2 \rightarrow HO_2$$
$$Fe^{+2} + HO_2 \rightarrow Fe^{+3} + HO_2^-$$
$$HO_2^- + H^+ \rightarrow H_2O_2$$
$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

In all fairness to the group working with Burton (*33*) and Allen (*34*) on the classified metallurgical project at the University of Chicago, these free radical mechanisms were widely used in the years, 1942–46, to interpret their water decomposition studies. Allen (*34*) in his comprehensive paper published in 1946 discusses the mechanism of free radical formation from ions and the reactions responsible for the radiation induced stabilization of water. He also presents the reactions for "molecular product" formation in the regions of high free radical concentration by the reactions:

$$H + H \rightarrow H_2$$

and

$$OH + OH \rightarrow H_2O_2$$

Water stabilization results from the free radical initiated hydrogen–hydrogen peroxide recombination reactions:

$$OH + H_2 \rightarrow H_2O + H$$

and

$$H + H_2O_2 \rightarrow H_2O + OH$$

Several years elapsed before the full significance of Allen's molecular hydrogen and molecular hydrogen peroxide was realized by radiation chemists. And Fricke's $(H_2O)'_{act.}$ needed to be rediscovered.

Dosimetry

Radiation chemistry gave us G, defined as the number of molecules converted per 100 electron volts of absorbed energy. M/N, molecules reacted/ion pair, served us for half a century; the roentgen, r, served us for a quarter of a century; but now radiation chemists accept G, an empirical quantity to express radiation yields, as a matter of expediency. M/N and r, dependent on ionization measurements, were practical units to characterize the dosage delivered when feeble radiation sources were used. But since N and r must be measured in gases, they had no convincing reality in liquids. G is much better and particularly so for particle radiations. Here one knows the energy of the particle and the number of particles; consequently E, energy absorbed, is easy to calculate.

X-ray and γ-ray dosimetry proved more difficult than electron and heavy particle dosimetry because energy now must be measured by an absolute method in an aqueous solution. Fortunately intense γ-ray sources and Fricke's ferrous sulfate dosimeter were at hand. In 1953, Hochanadel and Ghormley (*35*), by calorimetric measurement, obtained a $G(Fe^{+3})$ of 15.6 (ferric ions/100 ev) for Co^{60} γ-rays. This yield has been confirmed by many workers and applies to ferrous sulfate oxidation in aerated 0.8 N sulfuric acid by hard X-rays, γ-rays, and 1–2 Mev electrons. $G(Fe^{+3})$ drops to 12.9 for tritium β-rays (~5690 ev) and to 5.2 for 5.3 Mev α-particles (*36*).

Radiolysis Products

A simultaneous development with dosimetry was the measurement of the free radical and molecular product yields. While Fricke estimated the yields of $(H_2O)'_{act.}$ and $(H_2O)''_{act.}$ in 1935, yields of free radicals did not appear until about 1952. These yields then were calculated from the yields of products formed during radiolysis and in order to determine the radical yield one needed to know not only the specific radical reaction but also the mechanism of the reaction. Summaries of free radical yields are given in several reviews (*36–40*). The number of water molecules decomposed is of the order of one per estimated ion pair in liquid water.

With the free radical yields known, real progress

can be made in the study of reaction mechanisms. The general radiolysis equation is:

$$H_2O \rightarrow H_2, H_2O_2, H, OH, HO_2$$

Under normal conditions of irradiation, to a close approximation, the above species may be considered initial products formed with the radiation yields, $g(H_2)$, $g(H_2O_2)$, etc. Then conventional homogeneous reaction kinetics can be applied to the data for the reaction under investigation providing a mechanism is known. Using these assumptions, great progress has been made in the study of a number of inorganic and organic reactions. Under simple conditions, relative free radical-solute rate constant ratios, valuable in kinetic studies, are measured. Reactions that have received treatment are: ferrous sulfate oxidation, ceric sulfate reduction, oxygen, hydrogen peroxide, deuterium, iodide, nitrite, nitrate, formic acid, acetic acid, glycine, alanine, and many inorganic-inorganic and inorganic-organic mixed solute combinations.

Much progress has been made in product indentification too. With the use of the analytical techniques of spectrophotometry, chromatography, radioactive tracers, and mass spectrometry, complex reaction products have been identified. An outstanding example of this development is the analysis of aqueous acetic acid reaction products (*41*).

Free Radical Reactions

Because X-rays, γ-rays and electrons generate more hydrogen atoms and hydroxyl radicals that escape primary recombination in regions of high ionization density than α-rays do, these radiations prove more effective than α-rays in promoting free radical reactions. No attempt will be made to give the details of the many reactions studied in the past ten years but Table 2 contains a list of some of the important hydrogen, hydroxyl, and hydroperoxy radical reactions in aqueous radiation chemistry. Notice how the hydrogen atom will reduce one ion and then the hydroxyl radical will reoxidize the reduced form. In these cases the radiation yields are low. In other cases the hydrogen atom, often through the intermediary formation of the hydroperoxy radical will oxidize ions (Fe^{+2}) and in other cases it will reduce ions (Ce^{+4}, Cu^{+2}, Fe^{+3}).

Radiolysis Product Yields

Chemical systems that measure radiation yields are given in Table 3. The simplified equations express the experimental yield, G(Product), in terms of the free radical and molecular product yields denoted by lower case g's in this table. The sum or the difference of certain systems give these basic yields. Starting with the oxygen reactions, note that g(OH) is obtained by the difference between the two peroxide yields (systems II–I), and that g(H) is given by the difference between the two ferric yields, (systems III–IV). g(H) is also obtained from the dissolved deuterium system, V. $g(H_2O_2)$ is uniquely measured by the ceric system, VI, and $g(HO_2)$ by the ferrous-cupric system, VII. Systems VIII, IX, and X, involving ferric ion and formic acid or methyl alcohol give us the sum, g(H) + g(OH). And the formic acid-oxygen system, XI, enables one to measure each of the molecular product and free radical yields. If hydrogen is determined, each of the systems including XII, boiling or bubbling water, provides $g(H_2)$. Unless each of the yields can be measured separately, the equation of material balance, XIII, helps to derive these radiation yields.

Theoretical Research

Diffusion kinetics research is keeping pace with experimental research. Homogeneous kinetics breaks down in the treatment of radical diffusion out of a "track" or "spur" when recombination of radicals or when reaction with the solute occurs. The theory of the track effect is being developed in a number of laboratories (*42–48*). Even with a one radical model, by assuming an original gaussian distribution of free radicals, and simultaneous diffusion or radicals, with radical-radical and radical-solute reactions, the theoretical fraction of radicals reacting with the solute agrees well with observed experimental fractions.

Little headway has been made in the theory of free

Table 3. Systems for Measuring Yields in Irradiated Water

	System	Simplified yield equations
I	O_2, Br^-	$G(H_2O_2) = g(H_2O_2) + \frac{1}{2}[g(H) - g(OH)]$
II	O_2, H_2	$G(H_2O_2) = g(H_2O_2) + \frac{1}{2}[g(H) + g(OH)]$
III	Fe^{+3}, O_2	$G(Fe^{+3}) = 2g(H_2O_2) + 3g(H) + g(OH)$
IV	Fe^{+2}	$G(Fe^{+3}) = 2g(H_2O_2) + g(H) + g(OH)$
V	D_2	$G(HD) = g(H)$
VI	Ce^{+4}	$G(Ce^{+3}) = 2g(H_2O_2) + g(H) - g(OH)$ $G(O_2) = g(H_2O_2)$
VII	Fe^{+2}, Cu^{+2}	$G(Fe^{+3}) = 2g(H_2O_2) - g(H) - g(HO_2) + g(OH)$ $G(O_2) = g(HO_2)$
VIII	Fe^{+3}, HCOOH	
IX	Fe^{+3}, CH_3OH	$G(Fe^{+2}) = g(H) + g(OH)$
X	Fe^{+3}, Cu^{+2}, HCOOH, O_2	
XI	HCOOH, O_2	$G(H_2O_2) = g(H_2O_2) + \frac{1}{2}[g(H) + g(OH)]$ $G(CO_2) = g(OH)$ $G(-O_2) = \frac{1}{2}[g(H) + g(OH)]$ $G(H_2) = g(H_2)$
XII	Boiling H_2O	$G(H_2) = g(H_2)$

XIII $g(H) + 2g(H_2) = g(OH) + 2g(H_2O_2)$

Table 2. Some Free Radical Reactions in Aqueous Solutions

Hydrogen atom	Hydroxyl radical	Hydroperoxy radical
$H + D_2 \rightarrow HD + D$	$OH + H_2 \rightarrow H_2O + H$	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$H + H_2O_2 \rightarrow H_2O + OH$	$OH + D_2 \rightarrow HOD + D$	$HO_2 + OH \rightarrow H_2O + O_2$
$H + O_2 \rightarrow HO_2$	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH$
$H + Fe(H_2O)_n^{+2} \rightarrow Fe^{+3}(H_2O)_{n-1} + OH^- + H_2$	$OH + Fe^{+2} \rightarrow Fe^{+3} + OH^-$	$HO_2 + Fe^{+2} \rightarrow Fe^{+3} + HO_2^-$
$H + Ce^{+4} \rightarrow Ce^{+3} + H^+$	$OH + HSO_4^- \rightarrow OH^- + HSO_4$	$HO_2 + Fe^{+3} \rightarrow Fe^{+3} + H^+ + O_2$
$H + Fe^{+3} \rightarrow Fe^{+2} + H^+$	$OH + Ce^{+3} \rightarrow Ce^{+4} + OH^-$	$HO_2 + Ce^{+4} \rightarrow Ce^{+3} + H^+ + O_2$
$H + Cu^{+2} \rightarrow Cu^+ + H^+$	$OH + Tl^+ \rightarrow Tl^{+2} + OH^-$	$HO_2 + Cu^{+2} \rightarrow Cu^+ + H^+ + O_2$
$H + I_2 \rightarrow H^+ + I^- + I$	$OH + I^- \rightarrow OH^- + I$	
$H + NO_2^- \rightarrow NO + OH^-$	$OH + NO_2^- \rightarrow OH^- + NO_2$	
$H + CH_4 \rightarrow CH_3 + H_2$	$OH + CH_4 \rightarrow H_2O + CH_3$	
$H + HCOOH \rightarrow H_2 + COOH$	$OH + HCOOH \rightarrow H_2O + COOH$	
$H + CH_3COOH \rightarrow H_2 + CH_2COOH$	$OH + CH_3COOH \rightarrow H_2 + CH_2COOH$	

radical formation in liquid water since Allen (*34*) published the simple mechanism:

$$\begin{array}{l} \text{radn.} \\ H_2O \longrightarrow H_2O^+ + e^- \\ H_2O^+ + \text{aq.} \rightarrow H^+_{aq.} + OH \\ e^- + H_2O \rightarrow OH^- + H \\ OH^- + H^+_{aq.} \rightarrow H_2O \\ \hline \text{Net result } H_2O \rightarrow H + OH \end{array}$$

There is not much question about the fate of H_2O^+. Almost certainly the hydroxyl radical is located near the site of the original ionization. More uncertain is the fate of the secondary electron, e^-. Samuel and Magee assume that the electron does not leave the field of the parent ion and that it eventually forms a hydrogen atom by charge neutralization with H_2O^+. Platzman (*49*), on the other hand, supports the idea that the hydrogen atom is created at a considerable distance from the parent ion mainly by subexcitation electrons. These electrons, coming from the primary ionization of water, lose energy by inelastic collisions. When the energy is reduced below the lowest excitation energy of water, these "subexcitation" electrons become solvated and form hydrogen atoms. But these electrons may have much higher cross sections for reaction with solutes or impurities than with water. Interactions of these electrons with formic acid and with oxygen have been postulated in reaction mechanisms. Difficult, indeed, is the distinction between these electrons and hydrogen atoms in reactions involving the transfer of single electrons. Magee (*50*) and Dainton (*51*) provide a comprehensive time scale of events occurring in irradiated water from the initial ionization and dissociation events to the completed chemical reactions.

Future Developments

In the next decade, contributions to free radical chemistry will be impressive and radiation chemistry research already carried out on an international scale will expand immensely. Much will be learned about the properties of transient species and absolute free radical rate constants will be obtained not only for hydrogen atom and hydroxyl radical reactions but also for a great variety of other free radical reactions. The electronic computers will find new uses in radiation chemistry but their most important use, at least for the immediate future, will be the solution of diffusion kinetics problems. These developments will stimulate activity at the theoretical level and much progress can be expected on the complex problems associated with the formation of free radicals from ionized water molecules and secondary electrons.

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Development of Current Concepts of Elementary Processes in Radiation Chemistry

A chemical equation relates only the stoichiometry of a process. For understanding of the reaction, of its rate, of its dependence on various concentration and environmental conditions, knowledge of its mechanism is desirable. The individual steps in that mechanism are called the elementary processes. However, a true description of an elementary process involves writing something more than a simple reaction, and the details often elude discovery and invite speculation and experimental test over many years.

The elementary processes which most invite our attention are those which appear susceptible to detailed theoretical treatment and experimental test. In the present stage of our endeavors, we are limited to mathematical approximations in very simple cases and to qualitative extensions, by analogy, to more complicated systems. A favorite tool of the theorist is a system made of protons, deuterons, and electrons. For that reason much attention has been addressed over the course of the past 25 years to such simple thermal reactions as

$$H + D_2 \rightarrow HD + D$$

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

(i.e., the H-atom induced para-ortho conversion of H_2), to photochemical processes like

$$H_2 + Hg^* \rightarrow 2H + Hg$$

(i.e., the mercury-photosensitized decomposition of molecular hydrogen), and a simple neutralization like

$$H_3^+ + e^- \rightarrow 3H$$

The last reaction, as we shall see, has special interest for the radiation chemist. However, it is also true that "classical" elementary processes (i.e., those known outside the area of radiation chemistry) are, in general, of great importance to him.

It is particularly important to stress that progress in radiation chemistry frequently involves the recognition of elementary processes, the existence and potentialities of which might not have been suspected were it not for the peculiarities of this branch of science. The search for elementary processes tempts the adventurous and challenges the persistence of the hardiest of experimentalists. The reward of courageous and resourceful speculation and test is the discovery of an occasional new process suggestive of goals attainable only by the techniques of radiation chemistry.

An elementary process in radiation chemistry is either purely physical (with ultimate chemical consequences) or a sort of mixture which has both physical and chemical aspects. This review is concerned, to a very modest extent, only with a few of the latter class of processes. The ideally described process is one which includes not only a complete description of geometrical arrangements of reactants and products but also a complete description of the energetics including the receipt of energy by the reactants, the energy state or states of the activated complex, and the energy states of the products. In most cases the present views represent merely a step on the path to such a perfect description. Consequently, some attention is also given to the history and necessity for future development of these ideas.

Some History

The years 1895, 1896, and 1898 have equal significance for nulcear physics and radiation chemistry, just as do the names of Röntgen, Becquerel, and Curie (*1*, *2*.) Their new concepts and new discoveries did not come into existence fully accoutered in new and shiny elegance. Instead, the initial brilliance often lay hidden and unsuspected below an overlay of older ideas which themselves had not been completely developed nor well appreciated. Nevertheless, new discoveries do impel explanation on more and more fundamental planes, and it is interesting to examine how attempt at understanding of these discoveries searched backward toward truly basic notions and forward toward new discoveries both experimental and theoretical.

The earliest notion of the chemical effect of ionizing radiation on matter was that it is catalytic. It was not too troublesome that catalysis itself was not understood at the time. The use of the word "catalysis" furnished a category of ignorance under which the phenomena of radiation chemistry might be classified and to which basic questions might be relegated until some clearer understanding emerged. That the choice of category was infelicitous was, at the time, unappreciated. Luckily, the search for fundamental notions regarding radiation chemistry did not wait on such clarification.

In 1907, it was remarked by Bragg that the ability of radioactive material to ionize the surrounding air and the ability to induce chemical reactions appeared to run hand-in-hand. In 1910, Marie Curie proposed that the relationship was not merely parallel but consequential, that in any substance affected by high-

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energy emanations, the act of ionization precedes all chemical effects. This was the first suggestion of the nature of an elementary process in radiation chemistry.

The identification of Lind with the area of radiation chemistry dates from that time. As a consequence, perhaps, of an earlier interest in photochemistry, he saw advantage in a unit of yield similar to the quantum yield. He defined a new term M/N, the number of molecules converted per ion-pair, now frequently called the the ion-pair yield and still of great utility particularly in problems involving the radiation chemistry of gases.[1] The employment of such a unit, of course, solved no problems. The correlations which quickly became apparent did, however, stimulate the search for truly elementary processes in radiation chemistry.

The Ion-Cluster Theory

The important ways that energy is conveyed from radiation to matter are by momentum transfer (principally, as in fast neutron irradiation) (*3–5*) and by excitation and ionization. Irrespective of the nature of the primarily impingent radiation, the primary particle with which the radiation chemist is most frequently concerned is a charged particle (e.g., an alpha-particle or electron) and the primary effect with which he is concerned is the distribution of resultant ionizations and excitations along the ionization track of that charged particle. Some of our views concerning these processes are the result of fairly recent discoveries.

In the initial development of ideas of elementary processes in radiation chemistry, the first concern was with the behavior of the ions. Lind observed that, irrespective of the nature of the gaseous system studied, M/N was in most cases a small number and frequently an integer. Furthermore, in many cases M/N was unaffected by temperature (over a small range) or by gaseous composition or even by pressure. It helped in interpretation of these chemical phenomena that the physicists of that era had been explaining some anomalous mobilities of gaseous ions in terms of the existence of ion-clusters, in which a single molecule-ion would have adherent to it one or more molecules, held by induced dipole forces. Lind saw a significance of this notion for chemistry and propounded a theory of the elementary process, for many years the dominating influence in radiation chemistry, called the ion-cluster theory.

In terms of our modern usage, Lind might have written his concept of the primary processes in a mixture of gases A and B in the form

$$\mathrm{A} \rightsquigarrow \mathrm{A}^+ + e^-$$
$$\mathrm{A}^+ + n\mathrm{B} \rightarrow \mathrm{A}^+\mathrm{B}_n$$
$$\mathrm{A}^+\mathrm{B}_n + e^- \rightarrow \text{Products}$$

For a single molecular species like acetylene he would have written

$$\mathrm{A} \rightsquigarrow \mathrm{A}^+ + e^-$$
$$\mathrm{A}^+ + n\mathrm{A} \rightarrow \mathrm{A}^+_{n+1}$$
$$\mathrm{A}^+_{n+1} + e^- \rightarrow \text{Cuprene}$$

In this latter case, n would be assumed to have a value near 20.

The EHT Theory

In the 1930's there emerged in the theory of reaction kinetics a new idea which came to be known as the theory of the activated complex and which proved, in the hands principally of Eyring and his associates, to be a very valuable tool for the quantitative examination of a variety of chemical reactions. It was natural that the rather odd situations presented by radiation chemistry should prove a particularly intriguing challenge. Eyring, Hirschfelder, and Taylor (*6*) examined the value of n in Lind's ion cluster theory by application of the partition-function form of the theory of the activated complex and came to the conclusion that any theory which demanded a high value for n could not possibly correspond to reality.

Instead, Eyring, Hirschfelder, and Taylor proposed a synthesis of ideas (which had been known but neglected) to account quantitatively for the alpha-particle induced para-ortho conversion of H_2 and the radiolysis of HBr. They suggested, on the one hand, the importance of an ion-molecule reaction such as

$$\mathrm{H_2}^+ + \mathrm{H_2} \rightarrow \mathrm{H_3}^+ + \mathrm{H}$$

On the other hand, they emphasized the existence of processes parallel to those of photochemistry; e.g., excitation

$$\mathrm{HBr} \rightsquigarrow \mathrm{HBr}^*$$

with ensuant decomposition of excited molecules to yield free radicals

$$\mathrm{HBr}^* \rightarrow \mathrm{H} + \mathrm{Br}$$

and free-radical chain reactions which proceed according to well-established kinetic principles (*7*). The latter aspects of the EHT theory had a very great influence on development of our concepts of radiation chemistry and did much to clarify our notions concerning reactions which proceed with high yield. Unfortunately, as is indicated by Hamill in another paper of this symposium (*8*), the significance of ion-molecule reactions for the radiation chemistry of gases was overlooked once again until the last few years. A contributing factor to this continued neglect of a very important aspect of radiation chemistry was the emphasis on condensed systems resultant from the needs of atomic energy development in World War II (*4*).

Even before the end of World War II, evidence had begun to accumulate that highly excited molecules produced by a process such as

$$\mathrm{M} \rightsquigarrow \mathrm{M}^+ + e^-$$
$$\mathrm{M}^+ + e^- \rightarrow \mathrm{M}^\ddagger$$

contribute importantly to radiolytic reaction. Lea (*9*) had essentially suggested such a possibility for the radiation chemistry of water and such views were already current regarding the mechanism of radiolysis in general—particularly the radiolysis of organic compounds (*4*).

Processes Ensuant on Ionization

The mechanism of a neutralization process such as

$$\mathrm{M}^+ + e^- \rightarrow \mathrm{M}^\ddagger$$

[1] In modern usage, the customary unit of yield is G, the yield per 100 ev of energy input or 100 ev yield. Unlike the M/N value, it has no theoretical significance.

is not so obvious as it may appear superficially. In particular, it is not apparent why a molecule such as $M^{\pm}$, which presumably possesses enough energy (in the appropriate state of excitation) to be practically instantaneously ionized, should survive long enough to decompose by rupture into free radicals

$$M^{\ddagger} \rightarrow R + X$$

By contrast a possible decomposition by rearrangement to yield stable molecules (a process frequently discussed in conventional kinetics)

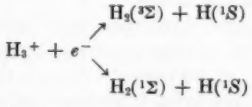
$$M^{\ddagger} \rightarrow A + B$$

seemed almost inconceivable.

The immediate approaches to solution of this problem were theoretical (*10*) and the initial choice of system was one involving protons, electrons, and their various combinations; e.g., H^+, H, H_2^+, H_2, H_3^+, and H_3, the latter of which exists only in repulsive states. One conclusion of this work was that a neutralization reaction such as that indicated at the head of this section almost invariably yields an excited molecule with energy insufficient for spontaneous reionization; the best evidence indicates that, even for a fairly dilute system of H_2 molecules, some of the energy released in the neutralization process is absorbed in polarization of the molecular environment.

The ion H_3^+ appears to have the perpendicular structure

An approximate calculation of part of the potential energy surface corresponding to the system $H_3^+ + e^-$ indicated the neutralization reaction to be one of two possibilities



with the reaction going almost invariably by the second process. The $H_2(^1\Sigma)$ formed (i.e., the H_2 molecule in its ground electronic state) possesses vibrational energy in excess of its dissociation limit and decomposes in one vibrational period (*ca.* 10^{-14} sec) to two H atoms

$$H_2(^1\Sigma) \rightarrow 2H(^1S)$$

On the other hand, in the rare cases when neutralization occurs by the first process, the $H_2(^3\Sigma)$ is in a repulsive state so that the effect is of an immediate dissociation into three H atoms with considerable excess kinetic energy

$$H_3^+ + e^- \rightarrow 3H$$

The latter reaction is also the over-all stoichiometric reaction but, in one sense of the term, represents an elementary process. We have seen, in this case, that a sophisticated treatment can be applied and that, when it is, details of increased understanding result. As a matter of fact, prior to the treatment of H_3^+ neutralization here described, it had been assumed on the basis of casual quantum mechanical considerations that the neutralization (and decomposition into atoms) went $^3/_4$ by the $^3\Sigma$ mechanism and $^1/_4$ by the $^1\Sigma$ path.

The considerations involving $H_3^+ + e^-$ were extended qualitatively to neutralization of polyatomic ions. The conclusion, of great importance for radiation chemistry, was that neutralization of such ions results with high probability in decomposition into two radicals one of which is excited,

$$M^+ + e^- \rightsquigarrow M^{\ddagger} \rightarrow R^* + X$$

In a succeeding paper of this series (*10b*), the conditions of negative ion formation, e.g., by simple capture

$$M + e^- \rightarrow M^-$$

and by dissociative capture

$$RX + e^- \rightarrow R + X^-$$

were examined and it was shown that positive ion neutralization was, in most cases, a more favorable process. In a later paper (*10c*), accretion of other molecules by the initial positive ion in straightforward chemical reactions prior to ion neutralization (*cf.* the Lind ion-cluster picture) was shown to have significant probability in certain cases. Reactions of such type may be important in radiation-polymerization.

Liquids and Related Systems

Excited Molecules

The conclusions regarding consequences of ion neutralization, recited in the previous section, apply with special force to gases. In liquids, highly excited molecules probably do not survive in a high state of excitation prior to decomposition. Luminescence studies (*11–13*) now teach us that highly excited states, such as those formed by neutralization, internally convert (with but few exceptions) to the lowest excited state allowed by the multiplicity selection rules (i.e., singlet or triplet) in a time of the order of 10^{-13} sec.

$$M^{\ddagger} \rightarrow M' \text{ or } M'''$$

It is reasonable to suppose therefore that radiolysis of organic liquids, insofar as it involves excited molecules (*cf.* the EHT theory section), involves only low excited states, regardless of whether they are formed in the initial act or indirectly after neutralization. Currently, there is considerable speculation and some experiment regarding differences in the fates of singlet and triplet excited molecules and the effects of various additives in controlling the rates of internal conversion reactions.

Protection. An excited molecule may give no apparent products because the free radicals produced are quickly captured by some scavenger. It may also fail to give products because it possesses an internal mechanism for dissipation of excitation energy (*cf.* unsaturated aldehydes in photochemistry). A third possibility is that the excitation energy is transferred from the excited region to some molecule or group which possesses a mechanism for dissipation of excitation energy. This latter phenomenon is called true protection (*14*) and seems to be fairly well established in some cases involving benzene or other aromatic compounds or groupings as additive (*15–17*).

An interesting point that luminescence and radiolysis studies teach is that even such compounds as cyclohexane appear to persist long enough after excitation that

they can actually be protected against decomposition by addition of a suitable additive. Only a small fraction of the energy transferred in such a protective act appears as luminescence of the receptor molecule. As may be suspected from fluorescence studies, such luminescence must always compete with other methods of energy dissipation.

Sensitization. The process of excitation transfer from an excited molecule to a receptor may not always be innocuous. If the receptor possesses no mechanism for energy dissipation, it may itself be chemically affected. Such processes of photosensitization are known in photochemistry but the elementary processes involved are not well established. Caffrey and Allen (*18*) have obtained preliminary results on a system of silica gel + pentane. Energy from gamma radiation absorbed in the solid lattice appears to be transferred specifically to the surface to induce a chemical reaction. Of course, additional work will be required to elucidate the mechanism. The term radio-sensitization itself means only that a molecule by its presence causes occurrence of a reaction or appearance of products which might not otherwise be found. The elementary processes involved in this case are yet to be established.

Water

During the 1920's, under the stimulus of James Franck, Göttingen became a meeting place for scholars interested in the potentialities and problems of photochemistry. Some of their concerns in liquid solutions were with so-called electron-transfer reactions, in which an excited molecule transfers its electron to one of a number of surrounding molecules or ions with ultimate results affecting both simultaneously (*19*). During the war years, Weiss, who had been in the Göttingen group, published a theory of the radiolysis of liquid water based on electron-transfer reactions which has for many years been the generally adopted, and doubtless controlling, view (*20*).

Essentially, the Weiss theory reduces to the notion that the only important processes occurrent in liquid water result from primary ionization (*9*) and that the effect of these processes is to produce H and OH separated from each other by the distance of a few molecules.

$$H_2O \rightsquigarrow H_2O^+ + e^-$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$
$$e^- + H_2O \rightarrow H + OH^-$$

Attempts have been made by Dainton (*21*) and by Laidler (*22*) to clarify the picture of the primary chemical processes in the radiation chemistry of water by description of the energy states involved, much as they have been described for the system $H_3^+ + e^-$. Such description is, of course, only inferential. The energy states of water are more or less known for the vapor. A description of the liquid system is necessarily largely one of analogy and based more on a hope that it will be helpful than on any expectation that it is necessarily correct. One result of such an approach is that it reveals the possibility of infrequently considered reactions. For example, Laidler suggests (in addition to the Weiss suggestions) such elementary processes as

$$H_2O \rightsquigarrow H_2 + O^+ + e^-$$
$$H_2O \rightsquigarrow H_2^+ + O + e^-$$

Of course, any theory useful in such an active field as the radiation chemistry of water cannot remain rigid. Thus, the original Weiss theory has always been in a state of flux. Weiss, for example, suggested the reaction

$$H + H_3O^+ \rightarrow H_2^+ \cdot aq$$

with the production of an essentially stable H_2^+ ion (*23*) with oxidizing properties; e.g.,

$$H_2^+ + Fe^{+2} \rightarrow H_2 + Fe^{+3}$$

The stability and even the independent existence of such an oxidizing species are a matter of current discussion (*24*). Hydrogen atom, or some "equivalent" entity, seems unquestionably to have a variety of oxidizing and reducing characteristics determined by the history of its formation (*24*). Some of these points are discussed elsewhere in this symposium (*25*).

The fascinating possibilities of the production of free radicals such as H and OH in aqueous solutions have been very extensively studied. Also, the possibility has been examined that other free radicals, such as HO_2, may be formed either in an initial stage or by interaction with solute, such as O_2. These are matters of special mechanism pertaining specifically to the behavior of water.

A very important concept, proposed by Allen (*26*), is that of a back-reaction chain

$$H + H_2O_2 \rightarrow H_2O + OH$$
$$OH + H_2 \rightarrow H_2O + H$$

which accounts for the substantial absence of detectable product, (i.e., H_2 or H_2O_2) in the radiolysis of γ-irradiated water. Such a result is to be contrasted with the readily detectable yields from α-irradiated water and, of course, did much to stimulate theoretical examination of the whole phenomenon. Two general avenues of approach should be mentioned.

In the first place, attempts have been made to examine carefully the primary processes preceding the first chemical effect. (*Cf.* Processes Ensuant on Ionization.) One conclusion important for the radiolysis of liquid systems in general was that electron capture (i.e., of electrons formed in ionization processes) to form either a positive ion or a negative ion occurs with high probability only after the electron is reduced to thermal energies. The conditions of competition to form positive or negative ions determine the nature and quantity of the intermediate species and, therefore, of the ultimate products.

Another more recent development has been the effort by Magee and his collaborators (*27–31*) to seek instead in the general theory of liquids for phenomena which may be found alike in a variety of substances. Essentially, their views derive from the concept of *spurs* of ionization and excitation distributed randomly along the ionization track like beads on a string.

The Spur and the Ion Track

The spur is the product both of the primary effect of the incident charged particle and of the secondary effect of an electron (i.e., a delta) resultant from a primary ionization act. The effects produced by such a delta depend on its energy and are known principally by analogy from studies of cloud-chamber photographs (*9*) and also from calculations of Kara-Michailova and Lea (*32*, *33*).

The average spur is thought in the case of hydrogenous substances to contain about three ions and about twice as many initially excited molecules. The diameter of the "average spur" is estimated to be about 20 Å for a hydrogenous liquid. Although the "average spur" contains three ions, the "typical spur" (corresponding to more than 40% of the cases) contains only one (*34*). Some recent, unpublished estimates by this author indicate that about one-quarter of such one-ion spurs contain also an initially excited molecule (probably triplet). In between the one-ion spurs there are also occasional excited molecules.

Two specially intriguing aspects of the radiation chemistry of liquids emerge from these considerations. In radiation chemistry, unlike photochemistry, an excited molecule is most likely found in the environs of another excited molecule. Thus, there is an important probability of reactions like

$$2M^* \rightarrow \text{Products}$$

Such a reaction is well-nigh impossible in any other branch of kinetics. Furthermore, the region from which a free radical escapes, if it is formed, contains initially, not two, but two or more *pairs* of free radicals formed by decomposition of excited molecules. This aspect of radiolysis is also unique.

Unlike the track of a fast-moving species such as an electron, the track of an alpha particle is practically a continuous column of initially ionized and excited molecules (*27*).

Free-radical Diffusion Theories in Liquids

The electron emitted in an ionization process is recaptured by the "parent spur" or column in a time $<<10^{-13}$ sec (*13*, *25*). Thereafter, unless some other trapping process such as negative-ion formation (*10b*, *13*) may be made to intervene, the electron is captured by the *parent* ion, or its equivalent, to yield a highly excited molecule (*13*, *27*, *28*). Both the highly excited molecule and the excited molecule have been thought to yield free radicals in a very early stage.[2] The significant reactions, according to this simplified view, may be written

$$M \rightsquigarrow M^*$$
$$M \rightsquigarrow M^+ + e^-$$
$$M^+ + e^- \rightarrow M$$
$$\left.\begin{matrix} M^* \\ M^\ddagger \end{matrix}\right\} \rightarrow R + R'$$

Our present views of the behavior of free radicals produced in radiolysis of liquids, largely the result of the theoretical work of Magee and his colleagues (*27–31*), are summed up in another paper of this symposium (*35*). It is sufficient to say here that a large variety of experimental tests, beginning with the results of Sworski on effect of Br^- ion (*36*) and extending into the effects of a variety of radiations on aqueous systems (*37*, *38*), are in substantial agreement with the quantitative predictions of Magee. Those predictions essentially involve the idea that the determining factor in the radiolysis of liquids is the initial distribution of excited species in the ionization track. The most recent results (*38*) suggest that a modification will be required of the current view that initially ionized molecules are the sole source of radicals in liquid water. That view has never been favorably espoused for organic liquids.

Recent considerations (*24*) suggest that for hydrogen-bonded systems, such as water, the initial decomposition may occur during the energy absorption act. However, in the usual liquids, such as represented by many organic compounds, excitation, ionization and neutralization (which may itself be complicated) are actually separate processes.

Electron Trapping and Neutralization

The electron emitted in an ionization process in a condensed system does not travel very far unless it be in a well-organized (e.g., ionic) crystal.[3] The electron is slowed down to thermal energies and trapped while it is still within the spur volume (*27*). However, the trapping need not involve neutralization of the parent ion. Once the electron is slowed to energies of the order of kT it may give negative ions either by simple capture or by dissociative capture (*10b*); e.g.,

$$O_2 + e^- \rightarrow O_2^-$$
$$RX + e^- \rightarrow R + X^-$$

Hamill, particularly, has indicated that liquids containing halogens, alkyl halides, etc., are especially susceptible to such type of reaction and that the radiolysis mechanism may be considerably modified in such cases because of the intrusion of the negative ion into the neutralization process (*13*).

Another point to recall about a condensed system is that a molecule is certainly, for about half its life or more, in a state of collision. Thus, the initial ionization processes may not only be

$$M \rightsquigarrow M^+ + e^-$$

but may also include

$$M,M \rightsquigarrow M,M^+ + e^-$$

When no negative ion former is around to interfere, the neutralization process occurs in $<<10^{-13}$ sec (*27*) and the energy released is sufficient to cause reaction between the two molecules which are still in a state of collision

$$M,M^+ + e^- \rightarrow \text{Products}$$

Perhaps processes like these or some modification[4] may serve to explain some of the phenomena involved in cross-linking of polymers (*40*). They bear a striking similarity to *Stern-Volmer reactions* such as are familiar in photochemistry (*13*).

Gases

In a discussion of our concepts of elementary processes, this paper returns fittingly to where it started—to mention of gases and the specific role of ions as emphasized first by Lind (*1*) and as modified, forgotten, and repeatedly reemphasized throughout the recent history of radiation chemistry by Eyring, Hirschfelder, and Taylor (*6*) and by others. This is the subject-matter of

[2] *Cf.*, however, discussions under "Excited Molecules" and "Protection."

[3] Considerations of such latter processes are specific for a certain class of phenomena usually encompassed in solid-state physics and are included in the subject matter of the review by Taylor (*39*) elsewhere in this symposium.

[4] For example, Magee has emphasized that the positive hole-electron pair may move very rapidly within the excited system before neutralization is complete.

another review (*8*). Here, it should be stated only that the approaches possible in a study of gaseous reactions in the ionization chamber of the mass spectrometer make possible almost direct observations of elementary processes, which even at the present time we know almost exclusively by remote inference.

* * *

A Note of Apology. In the title of this paper the word "SOME" is a saving grace. The author has not attempted an all-inclusive review. Neither has he attempted to state the "true" nature of any elementary processes. Rather he has attempted to indicate some of the paths by which some of the current concepts were attained. Even in such a slight task much has been omitted. In particular, since another paper of this symposium is addressed more particularly to aqueous systems by one who is considerably more expert in that field (*25*), he has neglected discussion of water to an otherwise unforgivable extent. The result has been the omission of a number of references to names which are literally beacons in radiation chemistry. There are likewise apologies due to many toilers in the field of organic liquids and, of course, to the many whom other participants in this symposium name in their respective reviews. The tribulation of the author is that, had he named specifically a few of these important contributors, he would have had increased cause to apologize to the rest.

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Errata

In "Textbook Error 21—Weathering Reaction" by Dan H. Yaalon in the February issue of this Journal there appear some slips of the not-caught-until-too-late variety. In the middle of the first column of page 74 the designation of "SiO_4 and AlO_4 groups" would be less confusing without the indication of charges. Careful readers will also find some compounds invented by type gremlins instead of the author, e.g., H_2SiO_4 instead of the correct H_4SiO_4, $NaAlSiO_3$ instead of the correct $NaAlSi_3O_8$, etc.

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Theoretical Foundations of Radiation Chemistry

Radiation chemistry is the chemistry of the effect of high-energy radiations on matter. These include high-energy photons (X-rays, gamma-rays) and high-speed material corpuscles (electrons or beta rays, protons, alpha-particles, fission fragments, etc.). The result of the absorption of such radiations by matter is the production of a variety of excited species, such as electronically excited molecules and ions in their ground or electronically excited states. Since the absorption phenomenon is a highly localized one, these species have a highly inhomogeneous spatial distribution. They are energetically unstable and undergo a sequence of transformations which terminate when thermodynamic equilibrium is re-established. The first set of transformations in the direction of this equilibrium produces the attainment of thermal equilibrium, but not of chemical equilibrium. The products of these transformations are stable molecules, some of which differ from those originally present, and chemically unstable species, such as free radicals. The next set of transformations consists of chemical reactions and diffusion involving the reactive species and produces, in the end, chemical equilibrium.

The over-all process, which starts with the bombardment of a material system by high-energy radiation and terminates with the re-establishment of thermodynamic equilibrium in that system, can be divided into three stages (*1*):

Physical stage, consisting of the dissipation of the radiant energy in the system. Its duration is of the order of less than 10^{-15} sec (*2*).

Physicochemical stage, consisting of the processes which lead to the establishment of thermal equilibrium in the system. Its duration is of the order of 10^{-12} sec.

Chemical stage, consisting of diffusion and chemical reaction of the reactive species leading to the establishment of chemical equilibrium. Its duration ranges from 10^{-8} sec upwards, depending on the rate constants, and diffusion coefficients of the reactive species.

Important contributions to the theoretical basis of radiation chemistry can be found in a large variety of related fields involving every one of these three stages. For example, all of molecular quantum mechanics, absolute reaction rate theory and statistical mechanics can be considered as part of these foundations. Consequently, it would be impractical to include in this paper a *complete* survey of the theoretical foundations of radiation chemistry. Instead, a choice will be made of a few theoretical problems which are typical of each of the three stages mentioned above and which, in the opinion of the author, have contributed significantly to the progress of radiation chemistry.

Before starting in this endeavor it is appropriate to mention that many excellent reviews on radiation chemistry have recently been published (*1–6*). In this paper, material was freely drawn from several of those reviews.

Presented as part of the Lind Jubilee Symposium on Development of Radiation Chemistry sponsored jointly by the Division of Chemical Education and the Division of Physical Chemistry at the 135th Meeting of the American Chemical Society, Boston, April 1959.

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The Physical Stage

As previously mentioned, this stage consists of the phenomena by which energy is transferred from the high-energy radiation to the system; it lasts not more than about 10^{-15} sec. As pointed out very clearly by Platzman (*1*), two different but related viewpoints can be taken in considering these energy absorption phenomena. From the first one, attention is focused on the incident radiation and one observes the rate at which it loses its energy. From the second one, attention is directed to the medium, and the nature and distribution of the initial species produced are considered. From the first point of view, the work of Bethe (*7*) is one of the theoretical pillars of radiation chemistry due to the insight it gives into this subject. A comprehensive monograph in this field was written by Bethe and Ashkin (*8*). We shall, in this section, consider both points of view.

Loss of Energy by Charged Particles

Heavy Particles. We will here review the derivation of Bethe's "semiclassical" expression for the rate of energy loss of heavy charged particles (protons, deuterons, α-particles) in matter. In this derivation the basic hypothesis is that the main mechanism of energy dissipation is by electrostatic coulomb interaction between the heavy particle and electrons of the medium. Actually, a small amount of energy is also dissipated by interaction with the nuclei of the medium.

Consider the situation in which a particle of charge ze ($-e$ being the charge of an electron) and velocity v is traversing a medium in which n is the number density of electrons (numerically equal to the number of electrons per unit volume of medium). Let this charged particle pass through the vicinity of an electron in the medium, b being the distance of closest approach. Let us assume that the mass and speed of the incident particle are sufficiently large so that the energy it transfers to the electron is small compared to its own kinetic energy, that its path is undeflected, and that its speed is unchanged by this collision. Finally, let the energy transferred to the electron be large compared to the energy with which this electron is bound to a molecule of the medium. Under these circumstances the momentum

p (product of mass by velocity) imparted to the electron can be easily calculated from classical physics. If x and y are the axis and t the time defined by Figure 1, then the following expressions can be written, according to classical mechanics:

$$p_x = \int_{-\infty}^{+\infty} F_x\,dt \qquad p_y = \int_{-\infty}^{+\infty} F_y\,dt \tag{1}$$

In these expressions, indices x and y denote x and y components of the imparted momentum p an the coulomb interaction force (attraction or repulsion) F. The

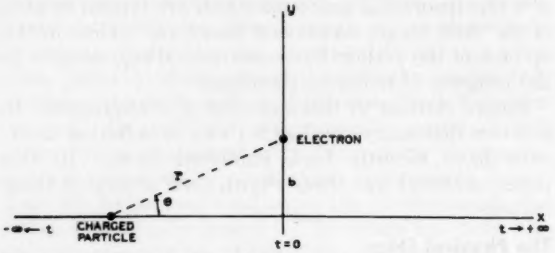

Figure 1. Trajectory of charged particle.

components of these quantities in the direction perpendicular to the paper is zero due to our choice of axis. From the figure and Coulomb's law it follows that

$$\left.\begin{aligned} F_x &= \frac{ze^2}{-r^2}\cos\theta = \frac{ze^2}{-b^2}\sin^2\theta\cos\theta \\ F_y &= \frac{ze^2}{-r^2}\sin\theta = \frac{ze^2}{-b^2}\sin^3\theta \end{aligned}\right\} \tag{2}$$

The integrals in equation (1) can be performed with the help of a change to the integration variable θ, which is related to t according to equation (3)

$$tg\theta = -\frac{b}{vt} \tag{3}$$

It will be assumed that the electron does not have time to move very much while the heavy particle passes close to it because of the high speed of this particle and hence the shortness of this passage time. This means that the quantity b can be considered to be independent of time in so far as equation (1) is concerned. Substituting equations (2) and (3) into equation (1) one gets

$$\left.\begin{aligned} p_x &= -\int_0^{\pi}\frac{ze^2}{bv}\cos\theta\,d\theta = 0 \\ p_y &= -\int_0^{\pi}\frac{ze^2}{bv}\sin\theta\,d\theta = -\frac{2ze^2}{bv} \end{aligned}\right\} \tag{4}$$

One may conclude from equations (4) that the imparted momentum, and hence the imparted velocity, is perpendicular to the trajectory of the charged particle and lies in the plane determined by that trajectory and the electron. The kinetic energy E_e imparted to the electron is then given by

$$E_e = \frac{p_y^2}{2m} = \frac{2z^2e^4}{mb^2v^2} \tag{5}$$

where m is the mass of the electron. In order to determine the total energy loss of the charged particle it is necessary to add up the energy losses due to interactions with all electrons of the medium. This can be done by considering a cylindrical shell of radius b, thickness db and length dx, around the particle track. This shell has a volume $2\pi bdbdx$; the decrease in the kinetic energy of the incident particle due to interaction with all the electrons in it will be $E_e n 2\pi bdbdx$. Integrating the contributions of all such shells between a lower limit b_l and an upper limit b_u of the parameter b there results the expression

$$-\frac{dE}{dx} = \frac{4\pi z^2e^4n}{mv^2}\ln\frac{b_u}{b_l} \tag{6}$$

The left-hand side of equation (6) is the rate of energy loss (energy loss per unit length) of the charged particle. It is also called instantaneous energy loss, stopping power, and linear energy-transfer (LET). Let us now examine these upper and lower limits. As b increases, the energy dissipated in the corresponding encounters decreases. At one point the binding energy of the electrons to the molecules of the medium can no longer be neglected, and the model used breaks down. As b decreases, the energy dissipated in the corresponding encounter increases, and eventually this energy is no longer negligible compared to the energy of the incident particle; once again the model breaks down. If the same problem is treated quantum mechanically (*9*), there results the expression

$$\frac{b_u}{b_l} = \frac{2mv^2}{I} \tag{7}$$

where I is a mean excitation potential for the electrons which increases linearly with the charges of the nuclei of the medium. For media which are elementary substances of atomic number Z the relationship is

$$\left.\begin{aligned} I &= 11.5Zev \quad \text{for } Z \leqslant 30 \\ I &= 8.8Zev \quad \text{for } Z > 30 \end{aligned}\right\} \tag{8}$$

Substitution of equation (7) into equation (6) yields

$$-\frac{dE}{dx} = \frac{4\pi z^2e^4n}{mv^2}\ln\frac{2mv^2}{I} \tag{9}$$

which is the famous Bethe formula. It breaks down when the velocity of the incident particle is too high or too low. For very high velocities, relativistic corrections have been worked out in detail, and can be found in Bethe and Ashkin (*8*). For very low velocities, ($E < 0.6$ Mev for protons and $E < 2.5$ Mev for alpha-particles), no satisfactory theory exists.

Electrons. If the incident particle, instead of being a heavy one, is an electron, the situation is only slightly changed. The main difference is that the factor 2 in the logarithmic term of equation (2) disappears because the reduced mass of the two electron system (incident electron and electron of the medium) is $^1/_2\,m$, whereas the reduced mass of the system consisting of a heavy particle and an electron is very nearly equal to the mass of the electron.

Another fact that must be considered is that both particles involved in the collision are electrons i.e., they are identical. After this fact is also taken into consideration, the rate of energy loss of incident electrons (*8*) is given by

$$-\frac{dE}{dx} = \frac{4\pi z^2e^4n}{mv^2}\ln\left(\frac{mv^2}{2I}\sqrt{\frac{\epsilon}{2}}\right) \tag{10}$$

where ϵ is the basis of natural logarithms. The velocity restrictions which must be obeyed for equation (10) to be valid are similar to those mentioned for equation (9).

A fast electron can also lose energy by a different mechanism. As its velocity vector is changed, when it

passes closer to a nucleus, it emits electromagnetic radiation called "bremsstrahlung." This however is usually a very minor effect in radiation chemistry (*1*).

Conclusions. Examination of equations (9) and (10) yields the following very useful conclusions. First, the rate of energy loss of a charged particle in a given medium is proportional to the electron density of that medium. This permits observations made in the gas phase, i.e., in Wilson cloud chambers, to be used to estimate parameters for condensed media, i.e., liquid water. This is how the interspur distances mentioned in a later section are obtained. Second, because the factor v^2 outside of the logarithimic term is more important than the one inside, the rate of energy loss increases as the particle slows down. Third, if we compare two particles of equal energy but different mass, the heavier one has a smaller velocity and hence has a larger LET (i.e., loses energy at a higher rate). As a consequence, the density of encounters along an alpha-particle track is several thousand times larger than that along an electron track of the same energy. This fact is of very great importance in the interpretation of the quantitative differences between the reactions induced by fast electrons and those induced by heavy particles, such as protons, deuterons, alpha-particles, etc.

Loss of Energy by High-Energy Photons

When high energy photons, such as X-rays and gamma-rays, pass through matter, they lose energy in three different ways: photoelectric absorption, in which the photon transfers its entire energy to an electron; Compton scattering, in which the photon transfers part of its energy to an electron; and pair production, in which the photon disappears, and a high-energy electron and positron are formed.

The theory of these processes has been carefully worked out. Their relative contribution to the total energy loss depends on the energy of the incident photon and the nuclear charges of the medium. For photons in the range of 100 Kev to 2 Mev (*10, 11*) the main mechanism of energy loss in water is by Compton scattering. The energy distribution of Compton electrons depends on the energy of the incident photons. For example, for 1 Mev photons (*10*), the energy of the Compton electrons varies from 0 to about 0.8 Mev having a mean value of 0.45 Mev.

A conclusion which can be derived from these facts is that the main effect of the absorption of high-energy photons by matter is the production of energetic electrons, which proceed to dissipate their energy as described previously. Thus, the theoretical conclusions mentioned above are of importance also in understanding the radiation chemistry of high-energy photons.

Effect on the Medium

The effect of transfer of energy from an energetic charged particle to the medium is to produce along its path a variety of excited species, such as electronically excited molecules and ions in their ground or electronically excited states, as well as free electrons. Also, together with the ions, secondary electrons of varying energies are produced. The electronic transitions by which these species are formed are "vertical transitions," i.e., occur in times (10^{-15} sec) which are short compared to molecular vibration times (10^{-12} sec). Little is known about the relative amounts of these species in the several electronic states, and much theoretical and experimental work remains to be done on this aspect of the physical stage. Some progress has been made in this direction for gaseous systems (*12*), but for liquids such as water the difficulties involved have not yet been overcome.

The Physicochemical Stage

As previously defined, this is the stage in which the excited species formed in the physical stage reach thermal equilibrium. It lasts about 10^{-12} sec, which is of the order of magnitude of molecular vibration times, during which internal molecular rearrangements can take place. The main difficulty involved in this stage is the lack of knowledge of the nature and distribution of the species produced in the physical stage.

During this stage, the excited ions and molecules dissipate their excess energy by bond rupture, luminescence, internal conversion, energy transfer to neighboring molecules, etc. Hence, the theory of these elementary processes is a part of the theoretical foundations of radiation chemistry (*13*). Lack of space does not allow us to go into this matter in more detail. It should be mentioned, however, that the theoretical work of Eyring *et al.* (*14*) on the interpretation of mass spectra is also pertinent to the physicochemical stage of radiation chemistry processes. Another phenomenon of importance during the physicochemical stage is the fate of the low-energy secondary electrons produced during the physical stage simultaneously with the positive ions by the high-energy charged particles. Let us examine only liquid water, which is one of the systems which has been most extensively studied. There are no direct experimental observations about the fate of these electrons. There are, however, two divergent theoretical views on this matter.

One of these views, proposed by Samuel and Magee (*15, 16*), assumes that the secondary electrons lose kinetic energy due to the electric attraction by the parent ion and the inelastic collisions with other molecules in which they lose a fraction λ of their energy per collision. Assuming that classical laws are obeyed, they derive the relationship

$$\frac{dE}{dr^2} = \frac{\lambda E}{L^2} - \frac{e^2}{2Dr^2} \tag{11}$$

between the kinetic energy E of the electron and the distance r from the parent ion. In equation (11), $-e$ is the electronic charge, D is the dielectric constant of the medium, and L is the mean free path of the electron. The time it takes for the electron to be recaptured by the parent ion is calculated by integrating equation (11) numerically and feeding the results into the expression

$$= \left(\frac{m}{2}\right)^{1/2} \int_{E=E_0}^{E=0} \frac{dr^2}{LE^{1/2}} \tag{12}$$

where m is the electron mass. For an initial energy E_0 of 15 ev, a value of $\lambda = 0.025$ and a value of D of 3, the value of t turns out to be 2.8×10^{-14} sec. This low value of D was taken rather than the normal value 81 because the dielectric relaxation time of water is of the order of 10^{-11} sec, which is much longer than the recapture time. As the electron is recaptured, the parent ion is transformed into an excited neutral molecule

which can then decompose into H and OH radicals produced close together.

According to the other view, proposed by Platzman (*16, 17*), such a simplified classical description does not apply. Instead, the electron loses its energy by causing vibration of the bond dipoles and rotation of water molecules. The dipole vibration loss brings the energy of the electron down to about 0.2 ev in about 10^{-12} sec at a distance larger than 50 Å from the parent ion. At this stage it will be surrounded by water molecules corresponding to the infrared value of the dielectric constant of about 5. It then continues to lose energy by excitation of rotation of water molecules, until it is thermalized in about 10^{-11} sec. Since that is the relaxation time of water, the electron cannot be recaptured by the parent ion, becomes solvated, and produces a hydrogen atom according to

$$(1)\quad e_{aq}^- + \text{water} \rightarrow H + OH_{aq}^-$$

The parent ion dissociates according to

$$(2)\quad H_2O^+ \rightarrow H^+ + OH$$

Consequently, according to Platzman's model, in agreement with an earlier suggestion by Lea (*10*), the H and OH which result from a given primary ionization are quite far apart from one another, whereas according to Magee they are quite close together. The difference between the initial distribution of these radicals is represented in Figure 2 (*16*) and is important for the chemical stage of the process.

The Chemical Stage

During this stage, the chemically reactive species produced previously undergo chemical reactions as they diffuse away from the site where they were originally produced. Two important problems associated with this stage have been examined theoretically. One of them has to do with the question of the relative importance of ionic versus free radical reactions. The other is associated with the spatial inhomogeneity of the initial distribution of reactive species and is considered in the theories of diffusion kinetics.

Ionic Versus Free Radical Reactions

In the early days of radiation chemistry, S. C. Lind, studying the reactions induced in gases and gas mixtures by high-energy radiation, was able to interpret these reactions by an ion-cluster theory (*18*), according to which the ions formed were the sole instigators of chemical reactions. For the cases in which the number of molecules reacted was large compared to what could be expected from bimolecular reactions between ions and neutral molecules, this theory postulated that a clustering of neutral molecules around each ion took place due to the existence of polarization forces. This theory overlooked the fact that the energy expended by α-particles in creating an ion pair in air exceeded, by a factor of more than two, the ionization potential of either oxygen or nitrogen, suggesting that other processes than ionization were involved. In 1936, Eyring and co-workers (*19*) examined theoretically some simple gas-phase radiation-chemical reactions and concluded that in them reactions involving free radicals played an important role. The impact of this theoretical work had the effect of making most radiation chemists reject entirely the role of ionic reactants other than being intermediates in the formation of free radicals. However, some recent experimental work by Stevenson and Schissler (*20*) indicated that reactions between ions and molecules in the gas phase occur with cross sections 10 to 100 times larger than gas-kinetic cross sections. A little later, Schaeffer and Thompson (*21*) reinvestigated experimentally the radiation-induced exchange between hydrogen and deuterium and concluded that ions play a major role. The large value of the scattering cross sections of thermal ions by molecules was explained theoretically by Vogt and Wannier (*22*) as being due to polarization of neutral molecules by ions, and Gioumousis and Stevenson (*23*) explained the large cross sections for ion-molecule reactions also on the basis of polarization forces, using a classical model. As a consequence of these recent developments, the importance of ionic reactions in the radiation chemistry of gases is being re-established. Magee and Funabashi have theoretically reinvestigated the clustering phenomenon in irradiated gases (*24*) and concluded that under certain specific conditions, clustering could greatly affect the mechanism of gas-phase radiation-chemical reactions. Their conclusions must still be tested by adequate experiments.

It is still believed, however, that in condensed systems such as water the main reactive species produced in the physicochemical stage, which react in the chemical stage, are free radicals.

Diffusion Kinetics

The following remarks apply to liquid systems in which, at the end of the physicochemical stage, reactive species are distributed inhomogeneously in space. In particular we will consider the case of dilute aqueous solutions in which it is assumed that these reactive species are H atoms and OH-free radicals. Let us examine the case of dilute air-saturated ferrous solutions. The principal reactions which occur during the chemical stage are assumed to be (*4*)

$$(3)\quad H + OH \rightarrow H_2O$$
$$(4)\quad H + H \rightarrow H_2$$
$$(5)\quad OH + OH \rightarrow H_2O_2$$
$$(6)\quad H + O_2 \rightarrow HO_2$$
$$(7)\quad OH + Fe^{+2} \rightarrow OH^- + Fe^{+3}$$
$$(8)\quad HO_2 + Fe^{+2} \rightarrow HO_2^- + Fe^{+3}$$
$$(9)\quad HO_2^- + H^+ \rightleftharpoons H_2O_2$$
$$(10)\quad H_2O_2 + Fe^{+2} \rightarrow OH + OH^- + Fe^{+3}$$

The net result of these reactions is the oxidation of ferrous ions to ferric ions. An important question is that of the over-all kinetics of this mechanism. If the H and OH radicals were homogeneously distributed, the problem would be a relatively simple one. Since, in order to interpret the observed experimental facts, it is assumed that they are not homogeneously distributed (*10, 15*), diffusion processes occur simultaneously with the reaction processes. Lea (*10*) and Magee (*15*) assumed that the diffusion processes obey Fick's laws of diffusion (*25*) and that the elementary reactions obey ordinary second order rate kinetics. The important reactive species in the mechanism above are H, OH, O_2, HO_2, Fe^{+2}, and H_2O_2. The concentration of each one of these species is going to depend not only on time but also on the position inside the reaction vessel. The rate expressions that hold, according to the hypothesis above, are:

$$
\left.
\begin{aligned}
\frac{\partial[H]}{\partial t} &= D_H\nabla^2[H] - k_3[H][OH] - k_4[H]^2 - k_6[H][O_2] \\
\frac{\partial[OH]}{\partial t} &= D_{OH}\nabla^2[OH] - k_3[H][OH] - k_5[OH]^2 - k_7[OH][Fe^{+2}] + k_{10}[H_2O_2][Fe^{+2}] \\
\frac{\partial[HO_2]}{\partial t} &= D_{HO_2}\nabla^2[HO_2] + k_6[H][O_2] - k_9[HO_2][Fe^{+2}] \\
\frac{\partial[H_2O_2]}{\partial t} &= D_{H_2O_2}\nabla^2[H_2O_2] + {}^1/_2k_5[OH]^2 - k_{10}[H_2O_2][Fe^{+2}] + k_9[HO_2^-][H^+] - k_{-9}[H_2O_2] \\
\frac{\partial[O_2]}{\partial t} &= D_{O_2}\nabla^2[O_2] - k_6[H][O_2] \\
\frac{\partial[Fe^{+2}]}{\partial t} &= D_{Fe^{+2}}\nabla^2[Fe^{+2}] - k_7[OH][Fe^{+2}] - k_8[HO_2][Fe^{+2}] - k_{10}[Fe^{+2}][H_2O_2]
\end{aligned}
\right\} \quad (13)
$$

In these expressions, [X] indicates the concentration of substance X at the time t in a point of the water with coordinates x, y, and z, ∇^2 is the usual Laplacian operator,

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

D_x is the diffusion constant of substance X, and k_i is the rate constant of reaction i. At time zero the concentrations of O_2 and Fe^{+2} are known and are spatially homogeneous, the concentrations of HO_2 and H_2O_2 are zero in any region of the water, and the concentrations of H and OH are not directly known.

Equations (13) form a system of simultaneous nonlinear partial differential equations. If it were possible to solve these equations analytically, one would obtain the concentration of all reactive species as a function of time, position in the vessel, diffusion coefficients, rate constants, and parameters of the initial distributions of H and OH radicals. From this it would be possible to calculate the total amount of final stable products of the reactions. For example, the final amounts of Fe^{+3} and H_2 would be given, respectively, by

$$
\left.
\begin{aligned}
N_{Fe^{+3}} &= \int_0^\infty dt \int_V (k_7[OH][Fe^{+2}] + k_8[HO_2][Fe^{+2}] + k_{10}[H_2O_2][Fe^{+2}])dV \\
N_{H_2} &= \int_0^\infty dt \int_V {}^1/_2k_4[H]^2dV
\end{aligned}
\right\} \quad (14)
$$

where $\int_V$ indicates a three-dimensional space integral over the entire aqueous solution. To test this theory, one would compare these calculated values with the experimentally measured ones. This is the general formulation of the theory of diffusion kinetics (*26*).

In order to solve equations (13) the first thing that must be done is to choose the initial distribution of H and OH radicals. Since no direct observations on this are available, an educated guess must be made based on the theories developed for the physical and physicochemical stages of the reaction. Experimental cloud chamber observations are available for the distribution of ions in the tracks of alpha-particles and fast electrons in air. From these observations and the proportionality of the instantaneous rate of energy loss on the electron density of the medium, as developed in Bethe's formula (equation (9)), estimates can be made for liquid water. The conclusion is (*15*) that for fast electrons small spherical spurs of about six free radicals each are produced, separated by very large distances, and that for alpha-particles of energy 5 Mev or less these spurs

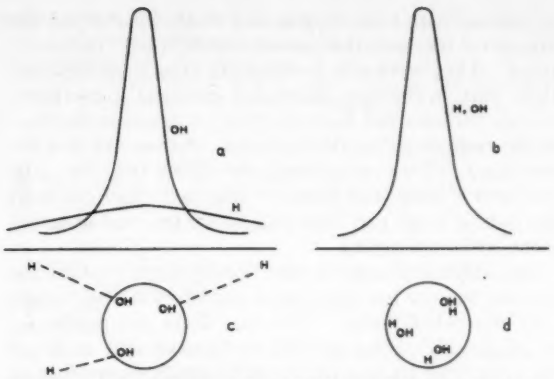

Figure 2. Initial distribution of H and OH free radicals according to Lea (a and c) and Magee (b and d). Reprinted from reference (*16*).

are so close together that a cylindrical column of free radicals is formed. In the fast electron case it is assumed that the interspur distance is so large that all reactions are essentially complete before the spurs overlap. In either case, at low dose rates (so that no track overlap occurs), each spherical spur or cylindrical track can be treated independently from all others. The fast electron case becomes one in which one space coordinate, namely the distance to the center of the spur, is sufficient to describe the variation of concentration with position. A similar thing happens in the alpha-particle case if it is further assumed that the density of free radicals does not vary along the axis of the cylindrical track. In this case, the distance to this axis suffices to describe the variation of concentration with position. The next step is to decide upon the dimensions of the spherical spurs and cylindrical tracks. According to Samuel and Magee (*15*), the dimensions of the spherical spur are of the order of 20 Å in diameter, both for H and OH radicals, and this is also the diameter of the cylindrical track considered to have infinite length. According to Lea (*10*) and Platzman (*16*), the OH radicals form spurs or cylindrical tracks of about 20 Å in diameter, but the H atoms are spread over a larger region (see Fig. 2) which Lea estimates to have a diameter of 150 Å whereas Platzman (*1*) thinks that it is much larger. In order to simplify the mathematics of the situation it is customary to assume that these initial distributions are gaussian, as indicated in Figure 2.

With the initial distributions thus chosen it should be possible, in principle, to solve equations (13). However, this cannot be done rigorously by analytical methods. As a result, in the initial days of the development of diffusion kinetics, certain mathematical simplifications (as opposed to the physicochemical simplifications introduced up to now) were introduced. For example, Samuel and Magee considered the case of pure water (no solute present) and assumed that H and OH radicals behaved identically. The only reactive step is then

$$R + R \rightarrow R_2$$

where R represents the H or the OH radical, and the diffusion-reaction equation involved is

$$\frac{\partial[R]}{\partial t} = D_R\nabla^2[R] - k_{11}[R]^2 \quad (15)$$

Since even this relatively simple equation is not soluble analytically, they further assumed that the distribution

of radicals maintains its gaussian shape throughout the lifetime of the spur (the "prescribed diffusion" model) or track. They were able to conclude from these assumptions that, in the case of isolated spherical spurs (high-energy photons and fast electrons), a non-zero fraction of the radicals diffused to infinity, whereas the rest recombined. They associated the latter fraction with the yield of molecular products and the former one with the radical yield, and were able to get reasonable agreement with experiment.

An additional step in the development of diffusion kinetics was the introduction of the effect of a scavenger into the calculations. This was done independently by Magee (*27*), Schwarz (*28*), and Fricke (*29*), at about the same time when it was experimentally shown that as the scavenger concentration increased the molecular yields could be drastically reduced. The mechanism invoked was

$$\begin{array}{ll} (11) & R + R \rightarrow R_2 \\ (12) & R + S \rightarrow RS \end{array}$$

where R represents the radicals and S the scavenger. The differential equations would be

$$\left.\begin{aligned} \frac{\partial[R]}{\partial t} &= D_R\nabla^2[R] - k_{11}[R]^2 - k_{12}[R][S] \\ \frac{\partial[S]}{\partial t} &= D_S\nabla^2[S] - k_{12}[R][S] \end{aligned}\right\} \qquad (16)$$

but, due to mathematical expediency, the second one of equations (16) was neglected and [S] was considered to be constant in space and time, i.e., D_S was considered to be infinitely large. This neglect of the scavenger diffusion (i.e., of scavenger depletion effects) was justified on the basis of the large excess of scavenger compared to the total amount of radicals present. These calculations agreed quite well with experiment (*28*) indicating that the basic ideas were probably correct. This agreement can be seen in Figure 3, in which the abcissa represent an adjusted scavenger concentration (which takes into account the difference of rate constants for different scavengers) and the ordinates represent the ratio of the amount of recombination in the absence of scavenger and that in the presence of scavenger.

The next step came with the use of high-speed digital computers. The first application was that of Flanders and Fricke (*30*) in which the first one of equations (16) was integrated by numerical methods under the assumption of lack of depletion effects mentioned above, for the same kind of spurs and tracks considered by Magee. The results were very close to the analytic approximate calculations. A further application was that of Dyne and Kennedy (*31*) in which two different kinds of radicals, H and OH, and one kind of scavenger were considered, depletion effects being neglected, with the initial conditions being that of Samuel and Magee's spherical spurs.

In a recent development, Kuppermann and Belford prepared a general program for integrating a general system of equations of the type of equations (13) on ILLIAC (high speed digital computer of the University of Illinois), for the cases in which a single space coordinate is sufficient for describing the variation of concentration with position (*26*). Other than that the program is quite general, permitting any initial distribution of radicals (e.g., Magee's, Lea's, or others), and including equations for the diffusion of scavengers as well as reactive intermediates initially present. In an initial application (*32*), the effect of scavenger depletion was studied. In it the solution of equations (16) for infinite D_S was compared with the solution for values of D_S of the correct order of magnitude. The conclusion was that for spherical Magee-type spurs and reasonable values of the physical parameters the depletion effect was never larger than about 1%. For cylindrical tracks of the same type, the maximum depletion effect found was 10% for 5.3 Mev alpha-particles and 20% for 1 Mev alpha-particles. Further calculations in progress involve the comparison between Magee-type and Lea-type spurs (i.e., effect of initial distribution) and the study of secondary reactions occurring in alpha-particle tracks. In this latter application one wishes to test the hypothesis recently put forward by Miller (*33*), according to which the reaction

$$(13) \quad OH + H_2O_2 \rightarrow HO_2 + H_2O$$

takes place to a considerable extent in 3.4 Mev alpha-particle tracks, although no H_2O_2 is initially present.

The future direction of the application of digital computer calculations to diffusion kinetics is to use programs of the kind just described to get a feeling for the influence of the several physical parameters on the final results, and to prepare programs applicable to situations in which two or three space coordinates are necessary to describe the variation of concentration with position so that the interaction between spurs may be investigated. Some approximate analytical work of this latter type has already been done by Ganguly and Magee (*34*).

Finally, a very important theoretical problem in connection with diffusion kinetics is the investigation of the validity of diffusion-reaction equations of the type of equations (13), along the statistical-mechanical lines followed by Monchick, *et al.* (*35*).

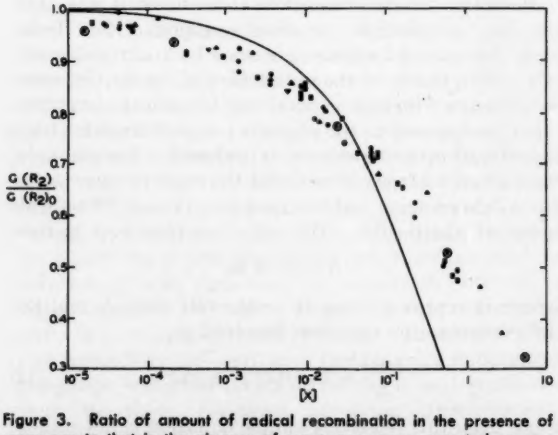

Figure 3. Ratio of amount of radical recombination in the presence of scavenger to that in the absence of scavenger versus corrected concentration of scavenger. Reprinted from references (28) and (3).

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(Continued in July)

Faint (Heart, Mind) Ne'er Won Fair Chemistry Student

(1) Ed and a coed sat in the cafeteria wondering about atoms and stuff.

(*a*) The coed looked down at the pin that Ed had just given her. She noticed the small inscription on the back of the pin that read "pure Al, weight: 2.698 g." She thought to herself "Let's see now, the atomic weight of Al is _____ so this pin contains _____ gram atoms of Al. If a gram atom of pure Al is worth 2 dollars, the Al in my pin would be worth (a little more, a little less) than a cup of coffee. I wonder if I should start dating a Kappa Sig or somebody."

(*b*) Ed tried to be both suave and impressive on this important occasion: He leaned over and whispered, "Now since the product of the specific heat and the atomic weight is approximately equal to _____, the specific heat of that beautiful pin must be about _____ cal/g/centigrade degree. And just think of it, soon the pin will be coated with a fine film of aluminum oxide so it will then be (heavier, lighter, the same weight). Of course, according to the Law of _____, only a limited amount of oxygen can combine with the Al in your pin. And according to the Law of _____, if 0.004 g of oxygen combines with the Al, the pin will weigh _____ grams. But if you should even think about dating a Kappa Sig, I intend to rub all the atoms off that remarkable pin with my bare hands. It may be a tough job, even for me, because there are _____ Al atoms in it and, incidentally, each Al atom only weighs _____ grams."

(*c*) A Kappa Sig at the next table was calculating frantically on his napkin. "Aha!" he exclaimed, "This may be my big chance. If Ed should rub a billion atoms per second off that pin, it would keep him occupied and out of circulation for _____ seconds. He (should, shouldn't) live so long."

Bonus Question (2 points): Moral of the story: It pays to know your (Chemistry, technique) at a time like this.

From a chemistry quiz by RALPH OLSEN
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Bozeman, Montana

R. J. Adams and **W. J. Blaedel**
University of Wisconsin, Madison

Electrodeposition of Silver and Copper Without the Use of Cyanide

The electrodeposition of silver and copper from alloys demonstrates several electrochemical principles and is an excellent experiment for the undergraduate course in quantitative analysis. Cyanide media are commonly used for electrodeposition of silver in the presence of copper (*3*). Quantitative separations, excellent deposits, and accurate results may be obtained. However, the poisonous nature of cyanide solutions is often a disadvantage. The toxicity of cyanide and difficulty in disposal prohibit its extensive use by undergraduate students.

This paper describes the investigation of other media for separating and depositing silver and copper. An efficient, accurate method for silver deposition was sought which would entail a minimum amount of time and chemical manipulation, and which would yield smooth, adherent deposits.

Since copper may be deposited from a much larger variety of solutions, the choice of media for silver-copper deposition is primarily limited to those from which silver may be deposited without interference from copper. After removal of silver, it is a minor problem to find suitable conditions under which the copper remaining in solution can be plated.

Ammoniacal solutions have been used extensively for silver depositions. Sand (*7*) obtained excellent results with ammonium hydroxide solutions at boiling temperatures and rather high current densities. Slomin suggested electrolyzing in hot, concentrated ammonium hydroxide solutions (*9*). High temperatures were employed to prevent the anodic formation of silver peroxide. Ethyl alcohol also suppressed peroxide formation. Miller (*6*) found that metallic silver appeared in solution toward the end of electrolysis in ammoniacal medium, but that hydrogen peroxide caused redissolution and ultimate deposition of the silver on the cathode. Miller further minimized metallic silver formation in solution by limiting the cathodic current to 1 ma/cm^2. Butler and Diehl used ammoniacal solution saturated with oxygen to prevent formation of the cuprous ammonia complex, which in turn caused formation of colloidal silver (*1*). The graded cathode potential method permitted accurate determination of silver in silver solders when oxygen was passed continuously through the solution (*2*).

Acetate media have also been used for silver deposition. Schleicher deposited silver quantitatively in the presence of copper from ammonium acetate-nitric acid solutions at boiling temperatures (*8*). Silver peroxide formation was prevented by elevated temperature and addition of toluol (*9*).

Smith found it possible to deposit silver in the presence of copper in nitric acid solutions containing a little alcohol (*10*). At 60°C, the deposition was accomplished in four hours. However, nitric acid media were unsatisfactory to other workers; silver formed large, loose crystals, and quantitative yields were not obtained (*2*).

The literature indicated that both ammoniacal and acetate solutions are satisfactory but did not permit a choice of either. Exploratory experiments were therefore performed in our laboratory, and these indicated the superiority of acetate over ammonia.[1]

Procedure

After dissolution of the alloy in concentrated nitric acid, water is added to give a volume of about 150 ml. Then concentrated ammonia is added until a permanent precipitate of silver or copper salts begins to form, indicating a neutral or slightly basic solution. The precipitate dissolves on adding 30 g ammonium acetate and 10 g ammonium nitrate. Electrolysis is carried out at 60–70°C, in tall-form beakers, and on a cylindrical platinum gauze cathode (5 cm × 5 cm diameter). A motor-driven rotating platinum gauze anode (4 cm × 2.5 cm diameter) gives good stirring. The deposition potential of silver is found in the solution, and the applied voltage is adjusted to give an initial current of about 0.8 ampere. As the electrolysis proceeds, the applied voltage is increased to maintain the current at about 0.8 ampere, until the applied voltage reaches a value about 0.4 volt more cathodic than the silver deposition potential. (The deposition potential of copper is about 0.6 volt more cathodic than that for silver.) Thereafter, the applied voltage is held approximately steady to avoid deposition of the copper. After the current reaches a constant value, the deposition is continued for another twenty minutes to insure complete deposition of the silver. The cathode is then rinsed with distilled water, rinsed with alcohol, air-dried for fifteen minutes, and weighed.

For the deposition of copper, the residual solution is acidified with 10 ml. of concentrated sulfuric acid. Copper is deposited onto the previously obtained silver deposit at room temperature and at an initial current of 0.8 ampere. The applied voltage is permitted to rise as much as 0.4 volt above the deposition potential for copper, since silver solders are free of interferences. The deposition of copper is continued for about a half hour after the blue copper-acetate complex completely disappears from the solution. Then the cathode is rinsed with distilled water and alcohol, air-dried for fifteen minutes, and weighed.

The above procedure was tested on solutions containing known amounts of silver and copper, with results shown in the table. Very good yields were obtained

[1] Fair results were obtained with high ammonium hydroxide concentrations (3 *M*), elevated temperatures (65°C), and ammonium nitrate as a cathodic depolarizer. Without nitrate, gas evolution occurred at the cathode, causing flaky, nonadherent deposits and low results for silver. Ammonium nitrate, hydrogen peroxide, and potassium permanganate were tried as depolarizers and, while these all inhibited the gas evolution, they also caused some oxidation of the silver deposit. Nitrate seemed most satisfactory, but even under the best conditions, yields of silver ranged only from 99.0 to 99.8%, and the quality of the silver deposit was not always good. Because of the elevated temperature, it was necessary to replenish the solution with ammonia as the deposition proceeded.

for both silver and copper. The silver coatings were smooth, white, and adherent. The copper deposits were smooth, adherent, and salmon-red colored, but showed some tendency to discolor after exposure to air. The procedure was also tested on several powdered silver solders containing 50–60% silver and 25–35% copper. Approximately one-gram samples were used, with yields comparable to those in Table I for both silver and copper.

Table I. Deposition of Silver and Copper in Ammonium Acetate Medium

Silver				Copper			
Present (g)	Yield (g)	(%)	Time (min)	Present (g)	Yield (g)	(%)	Time (min)
0.5008	0.5005	99.9	70	0.3000	0.3000	100.0	60
0.5168	0.5160	99.8	70	0.3115	0.3114	99.9	60
0.5019	0.5018	99.9	70	0.3784	0.3784	100.0	60
0.3117	0.3110	99.8	50	0.5914	0.5910	99.9	70
0.9884	0.9879	99.9	80	0.2998	0.2998	100.0	60
0.8736	0.8734	99.9	70	0.3486	0.3485	99.9	60

Selection of Conditions for the Deposition

The optimum temperature was 60–90°C. At lower temperatures, the deposition was not only slow, but the deposits were flaky. Gassing at the cathode was noted, indicating that the depolarizing efficiency of nitrate fell with decreasing temperature.

Several experiments were performed to find the optimum ammonium acetate concentration. Below 2 *M* ammonium acetate, the silver deposits became porous and less adherent. Above 2 *M* ammonium acetate, the characteristics of the silver deposit were not significantly improved.

The ammonium nitrate depolarizer prevents the evolution of hydrogen at the cathode during the deposition of silver, since nitrate is reduced more readily than water at the cathode (*5*). To determine the most effective concentration of ammonium nitrate, the potential difference between the "working" cathode and a saturated calomel electrode (S.C.E.) was measured (*4*). A Beckman *p*H meter was used as the potential measuring device since this instrument drew practically no current. The calomel electrode was bridged to the electrolysis solution with concentrated ammonium nitrate during the silver deposition in order to prevent precipitation of silver chloride. The potential of the cathode against the standard electrode was then plotted against time of electrolysis to follow the effectiveness of the depolarizer in maintaining the cathode potential at a constant value below that necessary for the decomposition of water. The curves in Figure 1 indicate that 10 g ammonium nitrate in 150 ml of solution depolarized the cathode sufficiently to prevent hydrogen evolution. Quantities of ammonium nitrate under 10 g permitted a drift in cathode potential after the initial rise caused by the deposition of silver. Quantities of ammonium nitrate above 10 g depolarized the cathode for a longer time than was necessary for quantitative deposition of the silver.

The best deposits were obtained at *p*H 7.5–8.0. Below *p*H 7.5, there was considerable gas evolution at the cathode, and the deposits were quite flaky and nonadherent. At values above *p*H 8.0, little gas evolution occurred, but the deposits were dark and nonadherent.

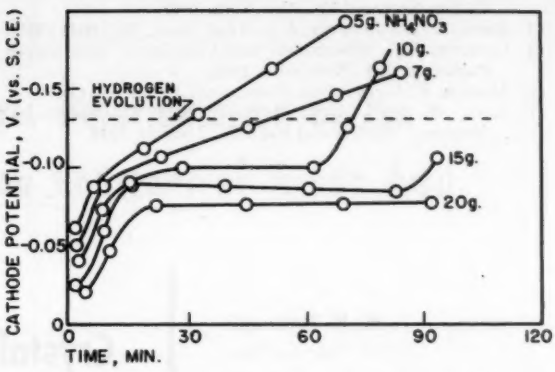

Figure 1. Cathodic depolarization by ammonium nitrate. Conditions: 150 ml of solution contained 30 g NH_4OAc, 0.5000 g Ag, 0.2500 g Cu, and varying amounts of NH_4NO_3. The current was maintained at about 0.8 amp by increasing the applied potential as electrolysis proceeded.

The time required for complete deposition of the silver was determined by titration of the supernatant with standard 0.05 *M* hydrochloric acid after various times of electrolysis. Fifteen minutes after the current had dropped to a constant value, less than 0.05% of the silver still remained in solution, while after 20 minutes, less than 0.01% remained.

Several of the silver deposits were redissolved in nitric acid, the silver was reprecipitated with hydrochloric acid, and the solution tested for copper with dithizone. Contamination of the silver deposit was found to be negligible, being slightly higher at higher temperature. At 90.0°C, the silver deposit contained about 0.05% copper, while at 25.0°C, only 0.01% copper was present.

A slight defect in the recommended procedure is that oxygen is evolved at the anode during the first fifteen minutes of silver deposition. Oxygen bubbles tend to be caught on the cathode, causing uneven deposition and slightly low results for silver (see Table 1). Occasional and momentary lowering of the beaker to clear the cathode of bubbles gave smooth deposits and quantitative results. When the cathode was not occasionally cleared of bubbles, results were low by as much as 1.0%. A rise in *p*H was found to accompany the oxygen evolution, but no means of preventing it could be found.

The principal source of error in the copper deposition is the cathodic liberation of nitrogen oxides, which increases the rate of redissolution of the copper. Some workers add urea to decompose these nitrogen oxides (*9*). Inspection of Table 1 shows that quantitative recovery of the copper is obtainable without the addition of urea. In fact, the addition of urea caused results for copper to be high by as much as 1.5%. The deposit was discolored, indicating that organic impurities were perhaps occluded when urea was present.

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Crystal Models

With the recent trend toward the structural approach in teaching general chemistry the need for large, nearly perfect crystals has become evident. Since the cost of such crystals would be prohibitive, the author turned to the construction of crystal models. Several criteria for such visual aids are evident: These crystal models should be large enough and strong enough to withstand classroom use, both at the lecture table and by the individual student. Furthermore, it is desirable that they be sufficiently accurate to permit analysis and interpretation of the crystal structures.

In order to meet this need, a set of models was constructed from about $25 worth of Plexiglas obtained through a commercial supply house for plastics. The raw stock obtained for this purpose consisted of both one-inch and two-inch thick sheet Plexiglas.

The models shown in the figure were sketched out on the plastic sheet and were roughly shaped by cutting the plastic with an eight-inch bench saw. This permitted the construction of all of the basic crystal forms which are usually encountered in a course of general chemistry. Where small faces were involved, these could be readily shaped by grinding the plastic on an ordinary carborundum wheel.

Crystal models made of Plexiglas. *Upper row:* simple cube, octahedral faced cube, octahedron, dodecahedron. *Lower row:* calcite, arragonite, octagonal prism, and quartz (hexagonal prism).

After the rough shapes were obtained, the most critical operation was polishing, achieved as follows: First, the rough faces were sanded down on silicon carbide No. 80 paper until the major irregularities were removed. The paper was placed on a flat surface. The plastic, held in one hand, was moved back and forth on the sand paper in order to produce a flat surface. Next, the plastic was finished up with No. 400 Wetordry paper—first dry and then wet. The surface of the plastic at this point was quite smooth but not optically clear. As a last step, the plastic was buffed with a canvas-covered disc treated first with white diamond buffing compound grade XXX, and then finished off with jewelers rouge. The resulting model was glass-clear, geometrically accurate to the extent required for the present purpose, and quite resistant to the scratches and abrasions encountered in ordinary use. As a precaution, however, the plastic should be treated as if it were glass insofar as its fragile nature is concerned, because corners can be chipped by dropping or by abrupt shock. However, the plastic models are considerably more resistant to breakage than ordinary glass.

It is estimated that about 30 hours of student labor were required to make the eight crystal forms shown in the figure. This student had no previous experience but, with a minimum amount of guidance, achieved the technique necessary to produce rather attractive models.

In addition to the basic crystal forms, several crystals representative of actual materials were prepared in order that some of their unusual characteristics could be illustrated. For example, one may identify in the figure a crystal of quartz, a simple cube, and a diamond. The quartz model was made large enough to show all the faces involved in this particular crystal, including the small faces which indicate either a right-handed or a left-handed quartz crystal. Since only the larger quartz crystals actually show these left- and right-handed faces, it is of considerable interest to the student to examine the models and arrive at the conclusions based upon his own observations. Models of a pair of calcium carbonate crystals in the forms of calcite and aragonite are found to be quite instructive when their actual shapes are compared to the internal molecular arrangement of the crystals themselves.

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Colorimetric Determination of the Dissociation Constant of Acetic Acid

Two years ago we found ourselves with the Bausch and Lomb "Spectronic 20" colorimeter in the undergraduate physical chemistry laboratory and nothing more exciting to do with it than to determine the absorption spectrum of some colored compound. Interesting experiments have been described[2] but they require an expensive spectrophotometer. A careful search of older literature revealed that a colorimetric investigation by Sidgwick, *et al.*,[3] dealing with the determination of the dissociation constant of acetic acid could serve as an interesting example of colorimetric technique, having the added virtue that it could be easily adapted to the requirements of a three-hour laboratory period with the colorimeter mentioned above. Following is a description of the modified experiment as used successfully for the past two years.

Principle of Method

The "color," or absorbancy, of a methyl orange solution is used as a measure of hydrogen ion concentration, from which the dissociation constant of acetic acid may be calculated. Absorbancy measurements are made at a wavelength greater than the isosbestic point of methyl orange (470 mμ), so that the yellow form of methyl orange absorbs less than the red form;[4] hence the absorbancy of the yellow form may be arbitrarily set equal to zero.[5] The experiment may be conveniently considered in two parts.

Part I. First it is necessary to determine the indicator constant K_{in}. As is well known, at *p*H above 4.4, methyl orange is yellow, and changes to red when the *p*H drops below 3.1. In a solution where $3.1 < p\text{H} < 4.4$, there will be an equilibrium

$$\underset{\text{acid color (red)}}{H_3O + HIn} \rightleftharpoons \underset{\text{base color (yellow)}}{H_3O^+ + In^-}$$

Hence the concentration of either the red or yellow forms, i.e., the "color," or absorbancy, of a methyl orange solution may be conveniently regarded as proportional to ionization. Let

A_s1 = absorbancy of a yellow completely dissociated solution of methyl orange;
A_s2 = absorbancy of a red undissociated solution;
A_s3 = absorbancy of any other solution, containing both dissociated and undissociated forms.

If the hydrogen-ion concentration of the solution is $[H_3O^+]$ gram-ion/liter, a fraction y of the indicator will be undissociated, and the absorbancy of such a solution will be given by the simple additive expression

$$A_s3 = yA_s2 + (1 - y)A_s1 \tag{1}$$

If K_{in} is the apparent dissociation constant of the indicator acid, then

$$K_{in} = \frac{[H_3O^+](1 - y)}{y} \tag{2}$$

Eliminating y between (1) and (2)

$$K_{in} = \frac{[H_3O^+](A_s2 - A_s3)}{A_s3 - A_s1} \tag{3}$$

This equation may be used for the experimental determination of K_{in} by measuring absorbancy at known values of $[H_3O^+]$.

Procedure: A stock solution $N/8000$ in methyl orange is prepared. Fifty milliliters of this solution is pipetted into each of three 250-ml volumetric flasks marked I, II, and III. Flask I is then filled to the mark with distilled water; this solution contains all of the methyl orange in its yellow dissociated form. Three milliliters of 1-normal HCl are pipetted into flask II and the solution is brought to the mark with distilled water. This solution contains all of the methyl orange in its red undissociated form (*p*H ≈ 2). Next 10 ml of buffer solution *p*H = 4.0 is pipetted into flask III, which is then filled to the mark with distilled water. This solution contains both dissociated and undissociated forms of methyl orange. The colorimeter is set for light of wavelength around 520 mμ, where the difference between the absorbancies of the red and yellow forms is largest,[4] and adjusted so that zero absorbancy is indicated for solution I, i.e., the absorbancies of the other two solutions are measured with reference to solution I as standard. With this setting, the absorbancies of solutions II and III are determined. Since by definition $A_s1 = 0$, (3) reduces to

$$K_{in} = \frac{[H_3O^+](A_s2 - A_s3)}{A_s3} \tag{4}$$

At least three sets of readings are taken.

Part II. The measurements on acetic acid are performed in the presence of dilute sodium acetate to repress the ionization of acetic acid. The dissociation constant of acetic acid is given by the equation

$$K_{HA} = \frac{[H_3O^+][A]}{[HA]} \tag{5}$$

The value of $[H_3O^+]$ in (5) can be obtained from (4) if K_{in} is known; A_s3 now refers to the absorbancy of an

[1] Now on leave of absence at the Department of Chemistry, University of North Carolina, Chapel Hill.

[2] (*a*) Phillips, J. P., J. Chem. Educ., **31**, 81 (1954). (*b*) Ish-Shalom, M., Fitzpatrick, J. D., and Orchin, M., J. Chem. Educ., **34**, 496 (1957). (*c*) Tobey, S. W., J. Chem. Educ., **35**, 514 (1958).

[3] Sidgwick, N. V., Worboys, W. J., and Woodward, L. A., *Proc. Roy. Soc.* (London), **129A**, 537 (1930). Sidgwick, N. V., and Woodward, L. A., *Proc. Roy. Soc.* (London), **130A**, 1 (1931).

[4] Fortune, W. B., and Mellon, M. G., *J. Am. Chem. Soc.*, **60**, 2607 (1938).

[5] It might be possible to use the Bausch and Lomb instrument in another experiment to obtain the spectral transmission curves for methyl orange at different *p*H values by a suitable modification of a laboratory experiment described in a very recent paper by Tobey[2c] dealing with methyl red.

acetic acid-methyl orange solution. However $[H_3O^+]$ so determined does not represent all the hydrogen ions furnished by the acetic acid because part of the hydrogen ions have combined with the indicator anions to form red undissociated molecules of indicator acid. If the solution contains 1 g-mole of indicator in v liters, and if y is the fraction of the total amount of indicator which is undissociated, then by (1) the concentration of the combined hydrogen ion [H^+ bound] is

$$[H^+ \text{ bound}] = \frac{y}{v} = \frac{A_s3 - A_s1}{A_s2 - A_s1} \times \frac{1}{v} \text{ gram-ion/liter} \quad (6)$$

The concentration of acetanion [A] in gram-ion/liter is obtained from the relation

$$[A] = [H_3O^+] + [H^+ \text{ bound}] + [NaA]$$

assuming complete dissociation of sodium acetate at the concentration used. The concentration of undissociated acetic acid [HA] in gram-mole/liter is given by

$$[HA] = [\text{total acetic acid}] - [H_3O^+] - [H^+ \text{ bound}]$$

Procedure: The following stock solutions are prepared: $N/8000$ methyl orange (from Part I), $N/100$ sodium acetate, $N/10$ acetic acid. 50 ml of the methyl orange solution and 50 ml of the sodium acetate solution are placed in each of three 250-ml volumetric flasks marked A, B, C. Then 50, 75, and 100 ml of $N/10$ acetic acid are pipetted into flask A, B, and C, respectively, and the flasks filled to the mark with distilled water. If the setting of the colorimeter has been left undisturbed from Part I, the absorbancy A_s3 may be determined directly for each solution. A_s3 may be determined directly for each solution. A_s2 is known, so that $[H_3O^+]$ may be calculated from (4). [H^+ bound] is obtained from (6) remembering that by definition $A_s1 = 0$, so that

$$[H^+ \text{ bound}] = \frac{A_s3}{A_s2} \times \frac{1}{40{,}000}$$

The values of $[H_3O^+]$, [A], and [HA] are substituted into (5) and the dissociation constant of acetic acid calculated for each of the three concentrations of acetic acid and an average value computed.

Student Results

The following results were obtained at room temperature at a wavelength of 485 mμ; better data may be expected at 520 mμ. Some care in the operation of the instrument is required, in particular watching for a possible drift in the zero setting for solution I.

Part I. Average of three determinations:

$$A_s2 = 2.02,\ A_s3 = 0.65;\ K_{in} = 2.1 \times 10^{-4}$$

compared with $K_{in} = 2.0 \times 10^{-4}$ reported by Glasstone.[6]

Part II. $A_s2 = 2.02$

Result	Solution A	Solution B	Solution C
A_s3	0.92	1.05	1.30
$[H_3O^+] \times 10^4$	1.8	2.3	3.8
$[A] \times 10^4$	21.9	22.4	24.0
$[HA] \times 10^4$	197	298	396
$K_{HA} \times 10^5$	2.0	1.7	2.3

The mean value is $K_{HA} = 2.0 \times 10^{-5}$ which checks reasonably well with $K_{HA} = 1.75 \times 10^{-5}$ at 25°C reported in the literature.[7]

[6] GLASSTONE, S., "An Introduction to Electrochemistry," D. van Nostrand Co., Inc., New York, 1942, p. 364.

[7] HARNED, H. S., AND OWEN, B. B., "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1950, p. 580.

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Titration Without Burets

There is a reluctance among some high school chemistry instructors to introduce titration experiments into the laboratory work performed by every student. The cost of the necessary burets, accompanied by the inevitable breakage by beginning students, often is a factor in deciding against such experiments. Even when they are used, burets present a cleanliness problem. A student setting up a titration assembly may get lost in a maze of inefficient fussing.

The suggestion here presented is that the use of a small polyethylene doll nursing bottle sold by five-and-ten-cent stores will teach the essential principles of titration without presenting any of the above objections. The embossed scale from 0 to 8 on the side of the bottle can be estimated to tenths of a unit. Consequently, if samples are so chosen that almost the entire scale is used for each titration, accuracy of 5% can be expected in beginning students' reports.

Although the bottle is not calibrated in milliliters, the scale division can be assigned milliliter dimensions. The error caused by this arbitrary assumption will cancel out in the subsequent calculations if concentration of unknown solutions is being sought.

Volumes delivered by the bottles can be measured if accurate calibration is desired. One interesting variation of this for the best qualified students would be to calibrate the bottle by using it to deliver a solution of known concentration to neutralize a known weight of a solid acid.

A polyethylene bottle is used to measure the acid strength of vinegar.

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Atmospheric Radioactivity Studies at the U. S. Naval Research Laboratory

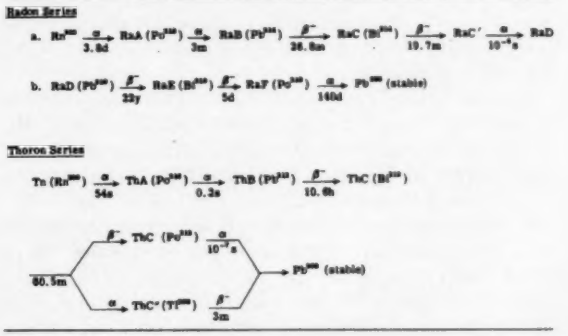
Early in 1948 the observation was made by personnel of the U. S. Naval Research Laboratory that gamma counters located on the ground at various places in the Northern Hemisphere showed a marked increase in gamma count whenever rain fell. This indicated the possible use of rainfall as a scavenger for airborne radioactive matter. It was known that there had been some atomic bomb tests in the Pacific and we suspected that the increase in count could be due to fission products, although the possibility existed that it could be due to the natural radioactivity always present in the atmosphere. In order to determine specifically what the activity was due to, it was necessary to obtain rain water that had been collected during the early months of 1948. A source of such water was discovered in the Virgin Islands where the entire water supply comes from rain. A large volume (2500 gallons) of this rain water from a cistern was treated with aluminum-hydroxide floc. Positive identification of the fission products Ce^{141}, Ce^{144}, and Y^{91} in the floc proved that the increase observed was due at least in part to fission products. A similar experiment using cistern water and plant material from Truk Atoll gave even higher fission product counts. Following this, experimental sites were set up in Washington, D. C., and Alaska early in 1949, and routine rain water collections from roofs of 1000 sq ft area were flocced and the floc examined for fission products.

No fission products at all were found in rain water from Kodiak but trace amounts were found in water collected at NRL. We naturally suspected Oak Ridge to be the source but decided to check our roof surface to see if it possibly were contaminated. Our Public Works people were certain then that all scientists were crazy when we requested a crew of laborers to scrub down our roof with brushes and to save the washings for us. However, from these washings were isolated thousands of counts (c/m) of the natural radioactive materials RaD, RaE, and RaF (Po^{210}) together with a few hundred counts (c/m) of cerium and yttrium activity. From the small amount of Ce^{141} present it was deduced that the source of this material was the atomic tests held the previous year. We immediately had a new aluminum roof installed and began collecting rain water free of the fission products. All during the spring and summer of 1949 no fission products were found in the rain, but in September of that year thousands of counts per minute of fission products were identified in the water from Kodiak, and hundreds of counts per minute in the water from Washington.

While this work was going on, nonchemical studies were being carried out to perfect a means of detecting low concentrations of fission products in the presence of the relatively high levels of natural radioactive material in the air. A physical method of analysis was soon devised which collected particulate matter from the air on efficient filters of small area, and demonstrated the possibility of identifying gross fission products through their effect on the rate of β-decay of the collected radioactivity.[1]

This NRL atmospheric radioactivity monitor equipment was designed for estimating the natural radioactive isotopes radon and thoron through measurements of their short-lived decay products, and determining the gross long-lived β-emitters in the air. The decay schemes of these materials are shown in Table 1.

Table 1. Decay Schemes of Radon and Thoron Series


Radon Series
a. Rn^{222} $\xrightarrow[3.8d]{\alpha}$ RaA (Po^{218}) $\xrightarrow[3m]{\alpha}$ RaB (Pb^{214}) $\xrightarrow[26.8m]{\beta^-}$ RaC (Bi^{214}) $\xrightarrow[19.7m]{\beta^-}$ RaC′ $\xrightarrow[10^{-4}s]{\alpha}$ RaD
b. RaD (Pb^{210}) $\xrightarrow[22y]{\beta^-}$ RaE (Bi^{210}) $\xrightarrow[5d]{\beta^-}$ RaF (Po^{210}) $\xrightarrow[140d]{\alpha}$ Pb^{206} (stable)
Thoron Series
Tn (Rn^{220}) $\xrightarrow[54s]{\alpha}$ ThA (Po^{216}) $\xrightarrow[0.2s]{\alpha}$ ThB (Pb^{212}) $\xrightarrow[10.6h]{\beta^-}$ ThC (Bi^{212})
β^- ThC (Po^{212}) $\xrightarrow[10^{-6}s]{\alpha}$
60.5m
α ThC″ (Tl^{208}) $\xrightarrow[3m]{\beta^-}$
Pb^{208} (stable)

Air is drawn through a stack from outside and passed through an efficient filter which effectively removes all particles greater than 0.3μ diameter. A G-M tube mounted directly above the filter gives an indication of the build-up of radioactivity on the filter. After 24-hour operation, during which 900–1200 cubic meters of air pass through the filter, it is transferred to a lead jug containing a similar G-M tube and its β-decay followed for the next 16 hours. Figure 1 shows a typical trace obtained during a collection. The rapid build-up is due to collection of the 26 minute daughter of radon (RaB). This activity is normally so high and so variable that it is generally impossible to identify the time of influx of fresh fission products into the area. Figure 2 shows typical β-decay curves of

Presented as part of the Symposium on Inorganic Chemists in the Nuclear Age before the Division of History of Chemistry and the Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

[1] Blifford, I. H., Jr., Friedman, H., Lockhart, L. B., Jr., and Baus, R. A., *J. Atmospheric and Terrest. Phys.*, 9, 1–17 (1956).

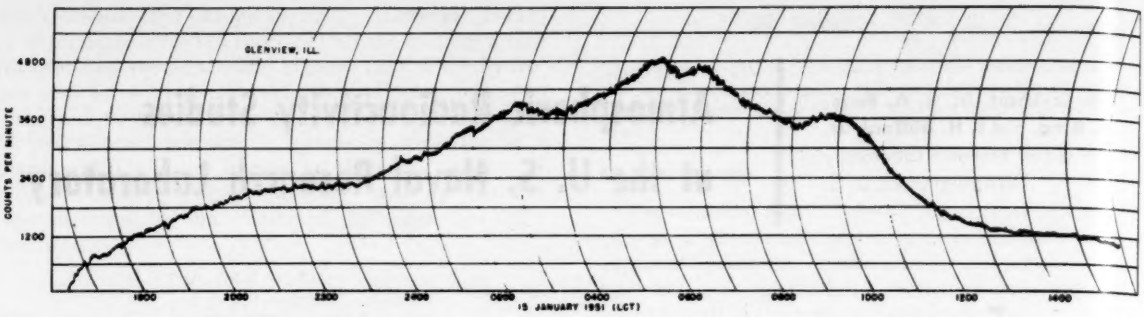


Figure 1. Recording of activity build-up during collection.

such collections, one consisting purely of natural products and the other containing natural materials plus fission products (20%). After 5 hours, the contribution of the radon daughters is negligible. From the ratio of the 6 to 16 hour counts or from the apparent half life of the mixture of longer-lived β-emitters, the contribution of both gross fission products and thoron decay products to the total activity may be calculated.

The next few years were spent in improving air monitoring procedures, working up more comprehensive procedures for chemical separations, and operating a small network of monitor stations at various naval installations. These latter stations have provided a continuous backlog of information on atmospheric radioactivity levels from the time when the detection of fission products was exciting to the present time when it is commonplace. During these years, one or more of these stations detected the airborne radioactivity resulting from every test series held in the Northern Hemisphere.

Routine rain water collections were discontinued when it was found that so much residual radioactivity from past tests continually leached off of our roofs that to continue in business, the collecting surface would have to be renewed after every test. This also led to the abandonment of a 10,000 sq ft collecting area which had been used to collect more massive amounts of radioactivity.

Data on the naturally occurring radioisotope RaE (Bi^{210}) and its relation to rainfall[2] have interesting implications. RaE is the 5-day daughter of the 22 year RaD (Pb^{210}), which itself results from the decay of the radon in the air. The rains appear to vary in their ability to cleanse the lower atmosphere as is indicated by the high activity levels sometimes encountered in the last part of the the rain. The lower efficiency of some of these may be due, in part, to the movement of "unclean" air into the area while the rain is falling. In general, it is apparent that the first part of the rain contains a higher concentration of RaE (or RaD). The dust content of this fraction is also high, but the RaE content has been found to be independent of the dust level.

A study of this type, combined with air-filter measurements of RaD and of the short-lived radon daughters, led to the conclusion a number of years ago that rain is the primary agent for removal of long-lived radioactivity from the air and, further, that the "mean life" of natural radioactivity in the air due to nonradioactive loss is about 15 days.[3]

Present Program

The present NRL program consists of two major projects. (1) the operation of air monitor stations of the type in use for the past 10 years and (2) the measurement of the latitudinal variation of the radioactivity of the air at ground level along the 80th meridian (west). This work is a part of the IGY program on Atmospheric Nuclear Radiation.

Table 2 presents the distribution of fission products and of the major natural radioactive isotopes in the air at several distinct geographical locations during 1957. Identical equipment is presently in operation

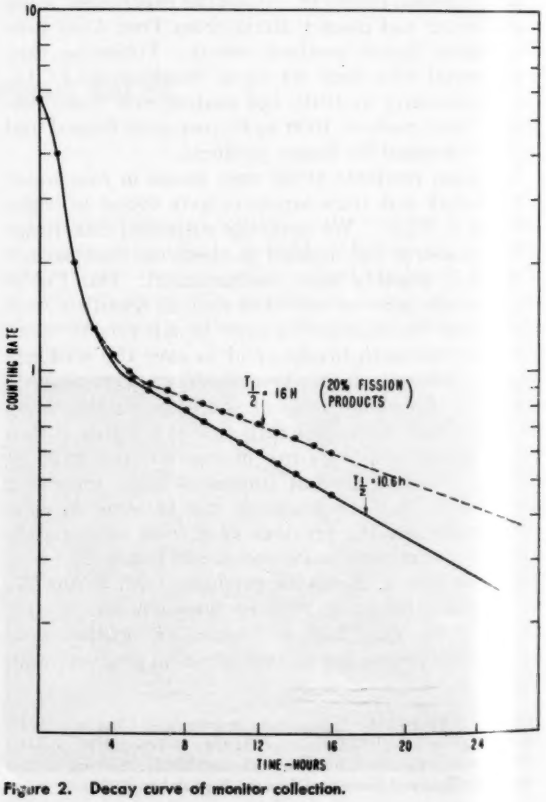


Figure 2. Decay curve of monitor collection.

[2] KING, P., ET AL., *Nucleonics*, **14**, 78–84 (1956).

[3] BLIFFORD, I. H., JR., LOCKHART, L. B., JR., AND ROSENSTOCK, H. B., *J. Geophys. Research*, **57** (4), 499 (1952).

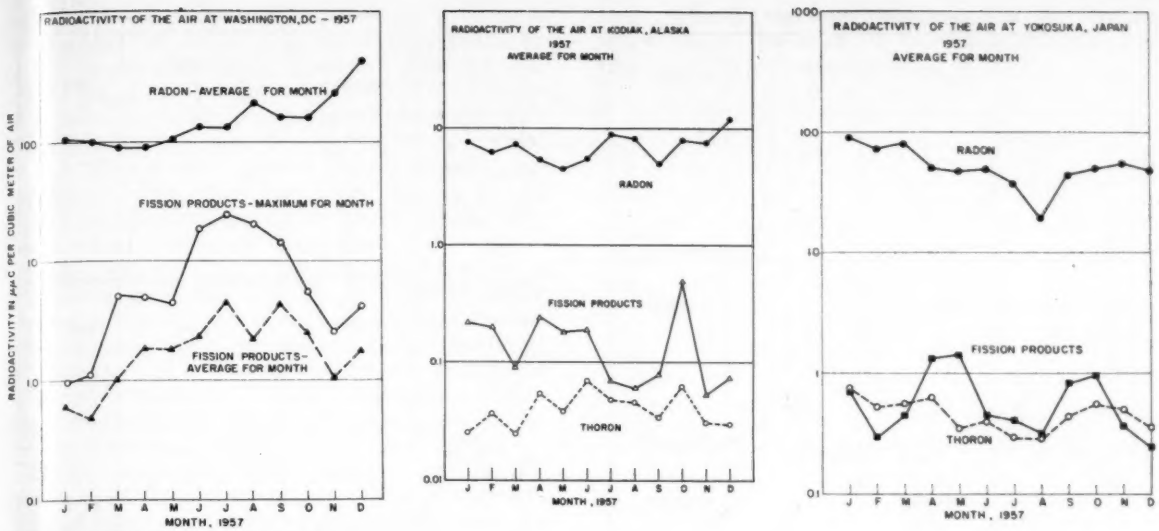


Figure 3. Atmospheric radioactivity levels.

also at San Francisco, at Rio de Janeiro, and at Chacaltaya, Bolivia, at the high altitude cosmic ray laboratory.

Table 2. Geographical Distribution of Atmospheric Radioactivity During 1957

	Activity in micromicrocuries per cubic meter[a]		
	Radon	Thoron	Fission products
Washington, D.C.	172	2.3	2.1
Yokosuka, Japan	54	0.48	0.66
Wales, Alaska	16.7	0.14	0.31
Kodiak, Alaska	7.3	0.042	0.16
Little America	1.5	<0.01	0.019

[a] 1 $\mu\mu$ curie/m^3 = 10^{-18} curies/cc.

Figure 3 shows the monthly variations in the natural and fission product activities at Washington, Kodiak, and Yokosuka during 1957. The large increase in gross fission products at Washington during July through September was due to our extensive series of nuclear tests in Nevada (PLUMBBOB). The maximum daily reading during the months is also presented on this graph and shows that even the peak fission product activity was much below the average radon level. Kodiak showed little response to these Nevada tests, but the fission product level increased markedly after the U.S.S.R. tests of August–October, 1957. At Yokosuka there were two peaks of activity that corresponded to the two series of U.S.S.R. tests with a definite lull during the period of our Nevada tests. In every case the average radon content of the air was 50–100 times that of the gross fission product level. In Figure 4 is shown a comparison of the variations in fission product levels at the different sites during 1957.

The second phase of our work, which is carried out as part of the United States contribution to the Nuclear Radiation program of the IGY, consists of the daily exposure at each of the collecting sites of the most efficient filters available. A simple air pump draws air through an 8-inch diameter filter paper at about 30 cubic feet per minute (1200 cubic meters per day). Local personnel at the cooperating site change the filters and return them to NRL via air. Here they are ashed at 650°C, compressed into 1-inch diameter discs, and counted under a thin-window G-M tube 14 days after collection. Sufficient counts are obtained on each sample to give a ±5% error at the 95% confidence level. The β-counting rates are converted to disintegration rates by the use of a factor derived from the counting rate of a radioactive standard mounted in

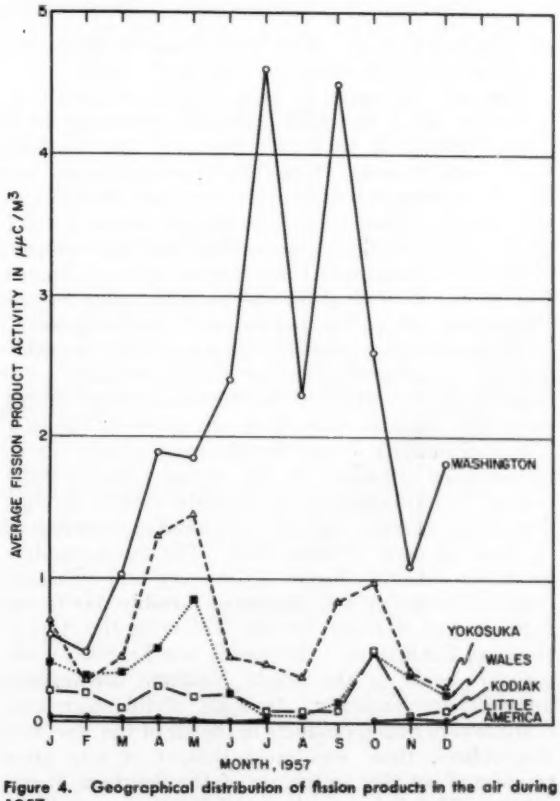


Figure 4. Geographical distribution of fission products in the air during 1957.

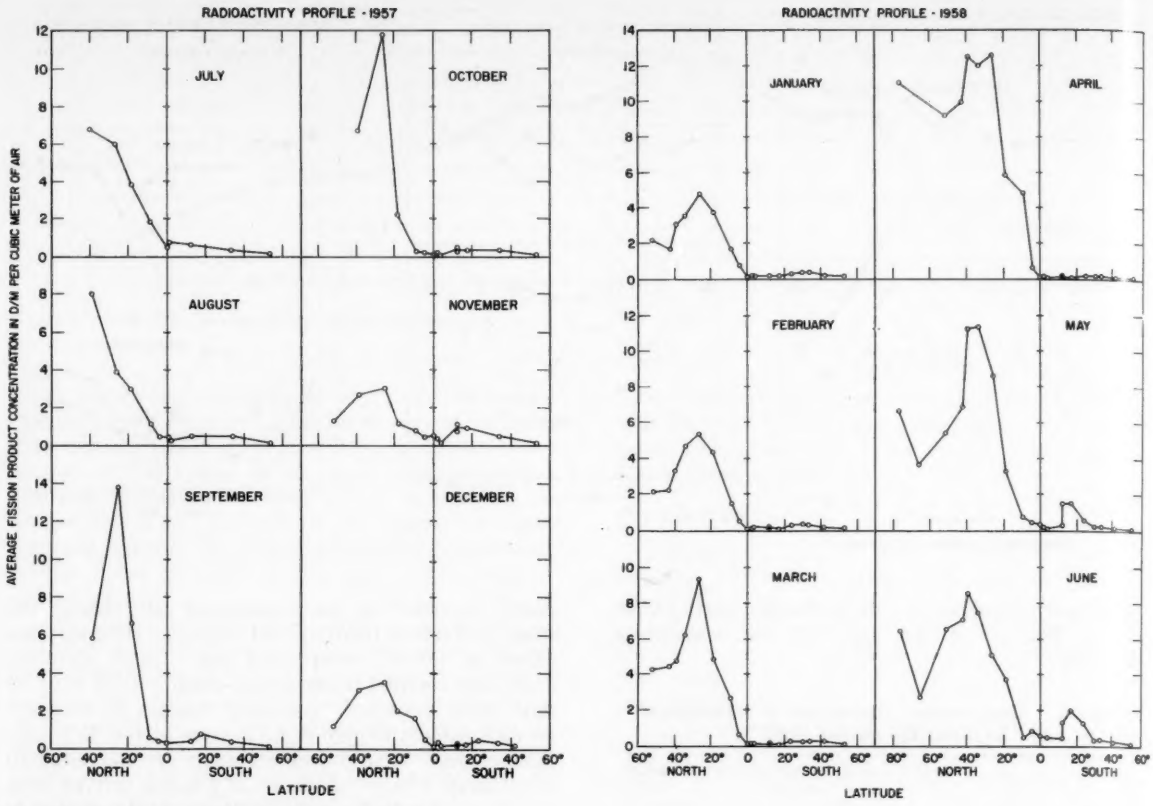


Figure 5. Radioactivity profiles, July 1957–June 1958.

an identical manner. The gross fission products are assumed to have an effective β-energy of 1 Mev.

Currently the complete network of 21 stations is in operation along the 80th meridian extending from Thule, Greenland, to Punta Arenas at the southern tip of South America. Some of these collecting stations have been in operation for over two years, though this IGY program itself officially started in January 1958. Other similar stations are operated by NRL as part of this IGY program at Pearl Harbor and atop Mauna Loa in the Hawaiian Islands, at Subic Bay in the Philippines, and on Drifting Station A in the Arctic.

"Radioactivity profiles" showing the monthly average air concentration of fission products as a function of the latitude of the collection station during July, 1957, through June, 1958, are shown in Figure 5. The radioactivity from Nevada tests is seen to be concentrated primarily in the region between 20°N and 40°N latitudes and to dissipate rapidly through deposition, dilution, and decay following cessation of the tests in early October 1957. The fission product levels were a little higher in January and February than in November and December possibly due to the U.S.S.R. test of December 28. Following the start of the large U.S.S.R. series of tests in late February 1958, activity levels in the whole Northern Hemisphere increased tremendously. In spite of this high concentration of fission products in the air of the Northern Hemisphere, there was no indication of any gross transfer of activity to the air of the Southern Hemisphere. The fission product activity there was shown by radiochemical analyses to be due primarily to more ancient tests and presumably resulted, in part, from the stratospheric deposition of old fission (or fusion) debris. The decided hump in the activity profile during May and June is due to British nuclear tests at Christmas Island with some contribution from our Hardtack series of tests in the Pacific. Our July measurements, however, showed a large increase south of the equator which must have been due to a massive transfer of activity across this barrier. For the first time, concentrations of fission products at some sites in the Southern Hemisphere exceeded that in the Northern Hemisphere.

A major portion of this IGY program presently involves the radiochemical analysis of monthly samples from each of the collecting sites. The samples are made up from the ash of the daily filters and, since these are asbestos-based papers, there is a considerable quantity of material to process. Carriers are added and the following isotopes separated: Sr^{89-90} (Y^{90}), Y^{91}, Cs^{137}, $Ce^{141,144}$ (Pr^{144}), and Pb^{210}. The Pb^{210} is included since it represents the principal long-lived natural radioactive isotope in the air.

Some information indicating the change in relative age of the debris with time is presented graphically in Figure 6. Here the percentage of the gross activity which is due to Sr^{90} is plotted for a series of monthly collections made at several sites along the 80th meridian. At the Northern Hemisphere sites (Panama, Miami, and Washington), the relative concentration of Sr^{90} was low during August–October because of the influx

of freshly fissioned material from Nevada. The rapid increase after October is due in part to the rapid decay of the shorter-lived fission products. However, the rate of rise is too high to be accounted for by decay alone and must be due to important additions of older fission products to the air masses sampled. Since the average lifetime of particulate matter in the lower atmosphere is less than one month due to natural deposition processes, the source of this excess long-lived material must be the stratosphere.

In the absence of new nuclear tests, the percentage of Sr^{90} in the gross fission products should gradually increase as the shorter-lived fission products die out. Eventually, the rate of decrease of the concentration of Sr^{90} in the air will be a measure of the rate of decrease of the concentration of Sr^{90} in the stratosphere. Thus a direct measure of the storage time of this material in the stratosphere can result.

The Sr^{90} versus gross fission product curves for two sites south of the equator are also shown in Figure 6. The high relative amounts of Sr^{90} indicate that the debris here are fairly old. Low Ce^{141} and Y^{91} activities confirm this. A decided dip in the percentage of Sr^{90} occurred in November following British tests in Australia (September–October) and at Christmas Island (November 8). The ratio increased to its previous high value in December indicating a fast wash-out of the fresh activity. This fast recovery of the atmosphere from such contamination was noted a number of years ago at our monitor stations in the Northern Hemisphere,[1] but it is no longer seen there.

It is our hope that information of the type presented here on the radioactivity of the air will serve, eventually, to help in the prediction of fallout, to determine mixing rates across the equatorial barrier and in the stratosphere and to determine the magnitude and residence time of Sr^{90} in the stratosphere.

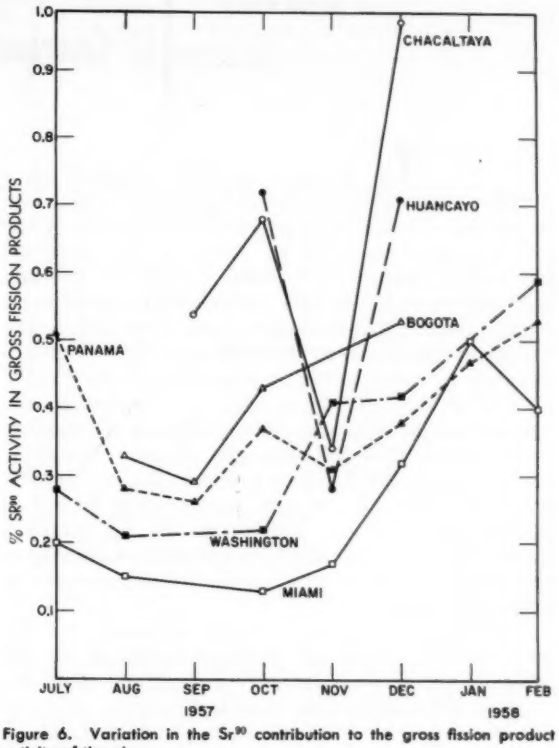


Figure 6. Variation in the Sr^{90} contribution to the gross fission product activity of the air.

MCA Honors Six College Chemistry Teachers

Six college teachers of undergraduate chemistry, considered outstanding in their field, are to receive the College Chemistry Teaching medals of the Manufacturing Chemists' Association, along with citations and awards of $1000 each. Their selection was made from among 157 candidates nominated from all parts of the country. Presentation will be made during the 87th Annual Meeting of the Association at the Greenbrier, White Sulphur Springs, West Virginia, June 11, 1959.

Recipients of the awards are:

James B. Culbertson, Cornell College, Mount Vernon, Iowa

Louis F. Fieser, Harvard University, Cambridge, Mass.

Roy I. Grady, College of Wooster, Wooster, Ohio

Hans B. Jonassen, Tulane University, New Orleans, La.

Louise Kelley, Goucher College, Baltimore, Md.

Richard E. Powell, University of California, Berkeley

E. M. Morimoto
and **Milton Kahn**
University of New Mexico
Albuquerque

Preparation of Carrier-Free Lead-212 (Thorium B)

The 10.6-hour lead-212 (thorium B), a member of the naturally occurring thorium series, can be separated in carrier-free form by collection of the active deposit produced by decay of the 52-second radon-220 (thoron).[1] A solid sample of thorium hydroxide or other suitable compound[2] is placed in an electric field. Thoron escapes from the solid into the gas phase where it decays to 0.158-second polonium-216 (thorium A) which, in turn, decays to positively charged ions of thorium B; these ions are collected on the negatively charged plate. Examination of the thorium series reveals that the separated thorium B will be contaminated with its decay products (i.e., thorium C, etc.). However, if enough time (~five hours) is allowed for transient equilibrium to be attained, determination of the total beta and gamma activity of the sample will serve as a measure of the quantity of thorium B present.

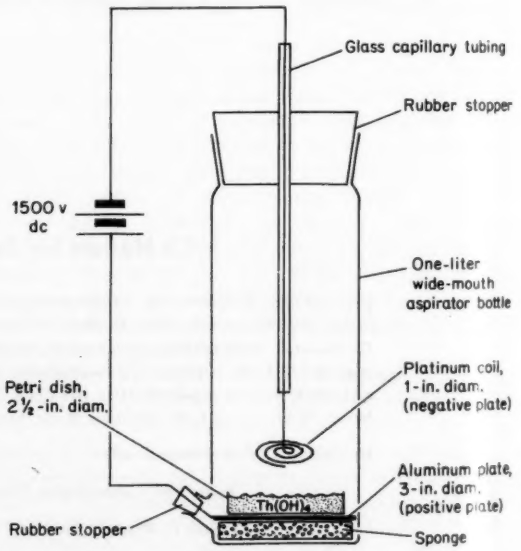
This paper describes a simple apparatus for the collection of carrier-free thorium B based on the aforementioned procedure. The amount of radioactivity obtained is more than sufficient to carry out experiments in the undergraduate physical chemistry laboratory.

The apparatus is shown in the figure. In operation, the rubber sponge is saturated with water in order to maintain the humidity at a high level. The platinum coil is adjusted to a height of about $^1/_4$ inch above the surface of the emanating source and a potential of 1200 to 1500 volts is applied across the plates. After a suitable collection period (~ten hours), the stopper assembly is removed and the activity is dissolved off the coil in 3 *N* nitric acid. The yield of thorium B is approximately 20%.

Effects of variations in voltage, plate separation, and humidity were investigated. The efficiency of collection increased from about 10% at 300 and 600 volts to 20% at 1200 volts; increasing the voltage to 1500 volts produced negligible gains. Varying the plate separation between $^1/_2$ inch and $1^1/_2$ inch resulted in no significant difference in the amount of activity collected as long as the voltage was over 1200 volts. The effect of the humidity of the atmosphere within the apparatus was pronounced. Increasing the relative humidity from 30 to 50% and 80% at 25°C produced, respectively, threefold and sevenfold increases in the efficiency of collection. Above 80% humidity, gains were not significant.

The thorium hydroxide used as the emanating source was precipitated from 400 ml of 0.036 *M* thorium nitrate. The precipitate was oven dried at 100°C for six hours and powdered with mortar and pestle. Because the 3.64-day radium-224 (thorium X) is not coprecipitated with thorium hydroxide it is necessary to allow time (~two weeks) for its growth in order to realize the 20% yield. During this time the emanating source is allowed to equilibrate with the moisture in the atmosphere in the apparatus.

The authors wish to express their gratitude to Dr. J. D. Knight of the Los Alamos Scientific Laboratory for valuable discussions.



Apparatus for collecting lead-212.

This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission.

[1] HEVESY, G., AND PANETH, F., "A Manual of Radioactivity," Oxford University Press, London, 1926, p. 90.

[2] WAHL, A. C., AND BONNER, N. A., *Editors*, "Radioactivity Applied to Chemistry," John Wiley & Sons, Inc., New York, 1951, p. 293.

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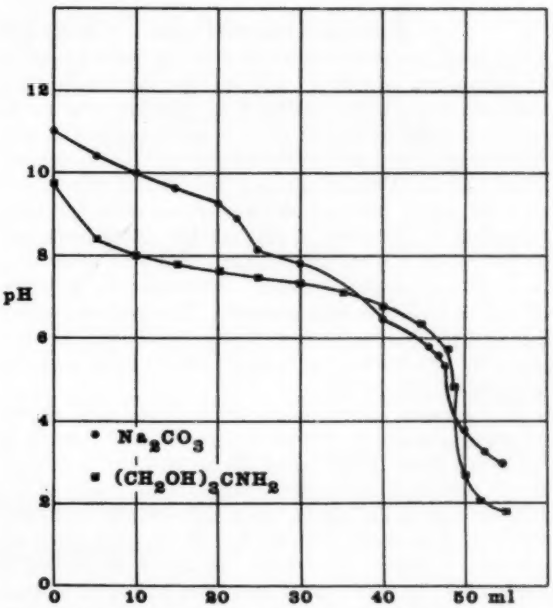
Tris(hydroxymethyl)aminomethane As a Titrimetric Standard

Sodium carbonate has long been the primary standard for standardization of dilute aqueous solutions of strong acids, and until recent years there has been no suitable substitute for it. In 1951, Fossum, Markanus, and Reddick (*1*) recommended tris(hydroxymethyl)aminomethane as a primary standard base for direct standardization of acid solutions, but it seems to have been overlooked by analytical chemists. It is mentioned in two texts published this year (*2*, *3*) but no details of its use are given.

The oversight of such a useful standard may be due to several reasons, other than academic inertia: The original reference (*1*) did not show a potentiometric titration curve to illustrate the *p*H range of the single stoichiometric point and compare it with the two stoichiometric points of sodium carbonate, although they did state that the stoichiometric point is at *p*H 4.7 (25°C); the authors (*1*) gave a method for purification of the compound and this may have suggested that it was not available commercially in a pure form; they listed several suitable indicators for use with tris(hydroxymethyl)aminomethane but these are less commonly used than modified methyl orange indicators.

Tris(hydroxymethyl)aminomethane, $(CH_2OH)_3CNH_2$, owes its basic properties to its amino group and reacts as a weak monoacid base, $K_b = 1.202 \times 10^{-6}$ at 25°C (*4*). It is a crystalline solid which can be weighed on tared watch glasses in air because it does not lose or gain weight. It may be dried in an electric oven at 100–103°C to insure purity. It is readily soluble in water, and such solutions are stable on storage for weeks because they do not absorb carbon dioxide. Since carbon dioxide is not absorbed, no boiling to remove carbon dioxide is necessary when titrating tris(hydroxymethyl)aminomethane with strong acid solutions.

The figure shows a potentiometric titration curve with 50 ml of freshly prepared 0.1000 *N* solutions of sodium carbonate and tris(hydroxymethyl)aminomethane against the same solution of approximately 0.1 *N* sulfuric acid at 25°C. It will be noted that tris(hydroxymethyl)aminomethane has only one stoichiometric point which occurs in the *p*H range 4–5, as does the second stoichiometric point of sodium carbonate. The use of methyl orange-xylene cyanol FF indicator gave equally good results with both titrations. Since the change from a green color to a steel-gray color with this indicator is a tricky one, a better indicator was found to be the mixed indicator of



Titration of sodium carbonate and tris(hydroxymethyl)aminomethane with 0.1 *N* sulfuric acid at 25°C.

bromcresol green-sodium alizarin sulfonate (alizarin red S) prepared as follows:

Triturate 0.1 g of bromcresol green with 1.5 ml of 0.1 *N* sodium hydroxide and dilute to 100 ml with distilled water. Dissolve 0.1 g of sodium alizarin sulfonate in 100 ml of distilled water. Mix the two solutions. Titrate to yellow color.

Tris(hydroxymethyl)aminomethane is now available in a pure form from Fisher Scientific Company as Certified Reagent T-395. This should not be confused with commercial grades which are available for organic syntheses.

It is believed that instructors and students will find this a very useful titrimetric standard.

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A Demonstration Model Illustrating the Aufbau Principle

The model described below was developed some years ago to demonstrate how, by the application of the aufbau principle, one can show the relationship between the relative energies of electron orbitals in many-electron atoms, the electronic structure of atoms, and the periodic table of the elements. It was demonstrated at the Bristol meeting of the British Association in 1955 and a preliminary description of it has been published.[1] The form of the periodic table presented in this model is virtually identical with that advocated recently by Longuet-Higgins,[2] who sets out fully the advantages of this arrangement. The present author can confirm that its successful use in elementary lectures given by him during the period 1948–54 fully supports Longuet-Higgins' views.

The general arrangement of the model is shown diagrammatically in Figure 1. In its final form it is built on a sheet of mild steel (26 in. × 42 in. × $^3/_{32}$ in. thick), set back from the vertical at an angle of 3°. (The original model used a $^3/_8$-in. plywood sheet which is more easily worked.) On the face of the back-plate are mounted a series of runways, as shown in Figure 1, made of $^1/_2$-in. wide brass strip and arranged so that a $^1/_2$-in. ball bearing placed at *A* (top right-hand corner) runs down to the bottom of the model. Certain sections of the runway (shown with a heavy line in the diagram) represent the possible energy levels of electrons and are arranged in an order characteristic of many-electron atoms. The front of the model is glazed with a sheet of plate glass on which are painted the symbols of the elements in the way indicated.

The tendency of an electron to occupy the lowest available energy level is represented in the model by the tendency of a ball bearing inserted at *A* to reach the lowest possible level in the model. Thus the first ball fed in runs down and occupies the space marked H, and represents the 1*s* configuration of the hydrogen atom. The second ball occupies the He space and the model then represents the $1s^2$ configuration of helium. The 1*s* level is now full and a gate at the exit from the 2*s* platform closes. In the first model (1949) this was achieved by a simple manually operated flap, while in the latest model (1955) the automatic device described below is employed. The next ball, therefore, is held in the lowest unfilled energy level and occupies the Li space: the model represents the $1s^22s$ configuration of lithium. On the addition of further balls the successive energy levels are filled in accordance with the aufbau principle, and at each stage the arrangement of the ball bearings gives the ground-state configuration of the element whose space is occupied by the last ball added. Apart from a few minor discrepancies, discussed by Longuet-Higgins, the configurations given by the model are in agreement with those accepted for the ground states of the elements.

In the earliest version of the model, overfilling of an orbital was prevented by flaps operated manually by levers mounted behind the plate. The model is much more striking, however, when arranged to work automatically. One convenient way of achieving this is illustrated in Figure 2. A number of light pivoted arms are mounted behind the back-plate, the ends of each arm being bent at right angles and brought through a slot to the front of the plate. The lower end of each arm is arranged to be operated by the final ball filling an energy level and to move the upper end of the arm down to block the exit from the next higher

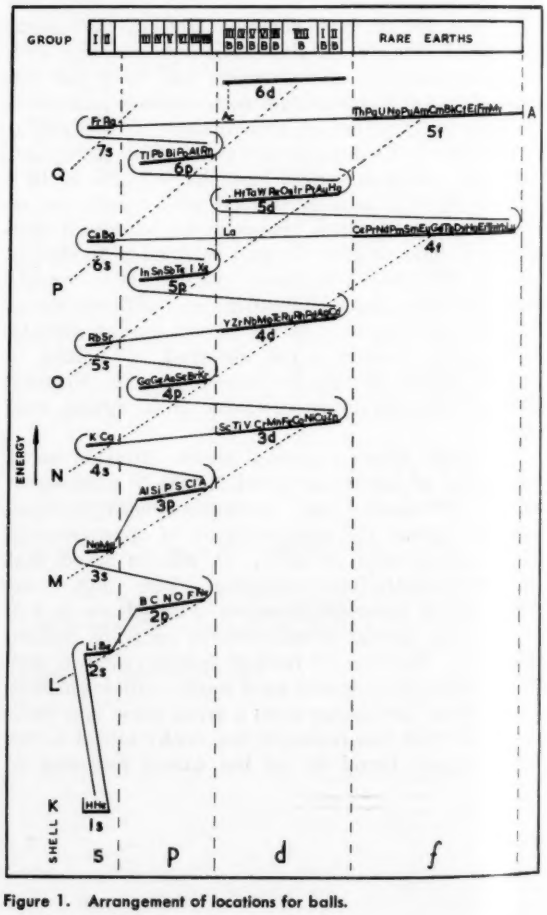

Figure 1. Arrangement of locations for balls.

[1] Everett, D. H., *Advance. of Sci.*, **13**, 515 (1956).
[2] Longuet-Higgins, H. C., J. Chem. Educ., **34**, 30 (1957).

level. Provided that the arms are carefully balanced and the balls are fed in one at a time with a 1–2 sec interval between them, this mechanical device works reliably and enables the whole periodic system to be built up automatically. The model is emptied by releasing a catch next to the H-position which allows the balls to run out through a hole in the back-plate.

It has been the author's experience that this model brings home in a convincing manner the concepts involved in the application of the aufbau principle, and that by setting up the electron configuration of the element whose properties are to be discussed in a lecture, the importance of the relationship between chemical properties and detailed electronic configuration is kept constantly in prominence.

Acknowledgment

The author is indebted to the late Mr. James Lackie of Dundee who constructed the original model and to Mr. H. Banwell and Mr. D. G. Yorke who devised the automatic gate and built the later model.

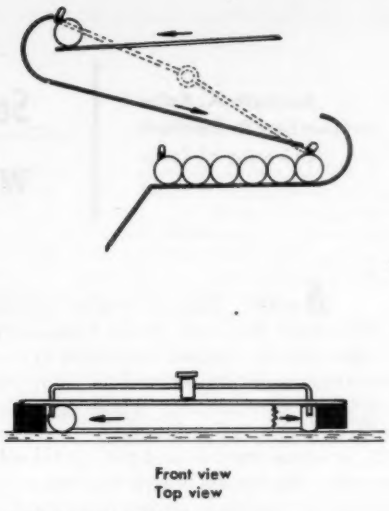

Figure 2. Mechanism for control of balls.

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Graphical Representation of Electron Configurations

A symbolism combining desirable features from methods in current use is suggested. It offers simplicity and clarity and facilitates the visualization of electron structure. It is flexible and readily adapted to show any amount of detail necessary for a particular discussion.

The number of electrons in each main electron shell is listed horizontally. When additional detail is desired for any particular shell, circles may be used to represent orbitals and arrows for electrons as shown in the following examples.

$$_{82}\mathrm{Pb};\ 2, 8, 18, 32, \overset{\textcircled{\uparrow\downarrow}}{18}, \textcircled{\uparrow}\ \textcircled{\uparrow}\ \bigcirc$$

conveys all of the necessary information more graphically than the customary representation ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^2$) and emphasizes the unpaired electrons with parallel spins in the $6p$ subshell. The upper circle represents the $6s$ orbital occupied by a pair of electrons spinning in opposite directions.

When details involving d orbitals are required, five circles are added below the three which represented the p orbitals. The electron configuration of iron may be shown in the following way.

$$_{26}\mathrm{Fe};\ 2, 8, \overset{2}{\underset{\textcircled{\uparrow\downarrow}}{6}}, \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}, 2$$

which graphically presents the important details of the $3d$ subshell while using numbers to represent electrons in filled shells and subshells.

Applying this method of representation to a transuranium element, all of the important features of the electron structure of americium are indicated by

$$_{95}\mathrm{Am};\ 2, 8, 18, 32, \overset{2}{\underset{\textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}\ \textcircled{\uparrow}}{10}}, 9, 1$$

which clearly shows the seven unpaired electrons in the $5f$ subshell.

It is sometimes convenient to substitute other symbols for the circles and arrows. In typewritten copy, the electron structure of iron may be indicated as

$$_{26}\mathrm{Fe};\ 2, 8, \overset{2}{\underset{\mathrm{NVVVV}}{6}}, 2$$

with the letters N and V representing orbitals containing paired and single electrons, respectively. These particular letters were selected because their shapes suggest double and single arrows.

When unoccupied orbitals are important, they can be indicated as shown in the following representation of niobium:

$$_{41}\mathrm{Nb};\ 2, 8, 18, \overset{2}{\underset{\mathrm{VVVVO}}{6}}, 1$$

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Separation of Organic Compounds with Urea and Thiourea

Around 1940, a German scientist accidentally discovered that urea would form a crystalline complex with various organic molecules (*1*). Several years later thiourea was observed to form crystalline complexes, of the same nature. These crystalline complexes, which are called adducts or inclusion compounds (*2*), are true crystals and not a solid solution or mixed crystals. Separation of hydrocarbon mixtures by the formation of adducts is an interesting subject that does not require special equipment for demonstration.

Examination of the crystal structure (*3*) of the adducts gives an indication of the manner in which the complex crystal forms. The host molecules, urea or thiourea, wrap around the guest molecule in a hexagonal spiral. The canal formed by the spirals of the host molecules is just large enough to accommodate the guest molecule. In a single macroscopic crystal many of these canals are situated side by side, each containing a molecule of the guest. The effective diameter of the canals is definite for the particular host, but the length varies according to the length of the guest molecule.

Consideration of the size of the organic molecule with respect to the canal size (*4*) will indicate if a particular organic molecule can fit into the canal and thus form an adduct. However, some general rules can be stated about which molecules will or will not form an adduct. Urea will form an adduct with long straight chain molecules which contain six or more carbon atoms. Thiourea is nearly complimentary to urea. It will form an adduct with branched hydrocarbons containing six or more carbon atoms and will also form adducts with certain ring compounds. Both urea and thiourea form adducts with straight chain compounds of about fourteen and more carbon atoms.

Adducts can be used for the separation of many types of mixtures of organic compounds (*5*). Compounds such as fatty acids, esters of fatty acids, alcohols, nitriles, etc., can be separated on the basis of the shape of the molecule according to the rules for urea and thiourea given above. They can also be separated on the basis of their chain length or of their degree of unsaturation. This is accomplished by taking advantage of the fact that a long chain compound will form an adduct with urea or thiourea in preference to a short chain. A chain length difference of about four to six carbon atoms is necessary to obtain the best results. For a mixture of molecules of various degrees of unsaturation, separation is based on preferential formation with molecules of the lowest degree of unsaturation. A quantity of urea or thiourea insufficient to adduct with all of the organic is used for this type of separation. The compounds that have preference will form adducts first leaving the others in solution.

Another interesting separation which can be performed with urea or thiourea adducts is that of a mixture of optical isomers. Usually these compounds have a very small boiling point difference which makes distillation difficult. A difference in the solubilities of the adducts of each isomer permits separation by using the insufficient urea or thiourea technique. The procedure requires a large number of repetitions, but it is a good method of separation for compounds that are sensitive to heat.

At the present time, urea and thiourea are in use commercially for the dewaxing of petroleum stocks for pour point improvement, for treating jet fuels, and for preventing air oxidation of fats by storage and shipment in their adduct form (*6*).

Laboratory Separation

Adducts are prepared by bringing the complexing agent, urea or thiourea, into intimate contact with the organic compound. As an example of a separation, 25 grams of thiourea are dissolved in 125 milliliters of anhydrous methanol. To the thiourea-methanol solution is added 5 grams of carbon tetrachloride which has been mixed with an equal weight of octanol or some other compound which does not form an adduct with thiourea. The mixture is shaken thoroughly and allowed to stand at room temperature. Needle-like crystals of thiourea-carbon tetrachloride adduct will begin to

Compounds Which Form Adducts at 25°C

With urea	With thiourea
Acetone	Carbon tetrachloride
Methyl ethyl ketone	2,2,4-Trimethylpentane
n-Heptane	Cyclopentane
n-Octane	Cyclohexane
Octanol	Cyclohexanol
Oleic acid	Cyclooctane
Methyl stearate	Decahydronaphthalene

The appearance of this article reminds Dr. Kobe's many friends of the deep feeling of personal loss which the news of his sudden death produced last November. The manuscript of this article was the last he edited himself.

KENNETH A. KOBE was a man of wide and varied interests. It was the good fortune of the present editor and his predecessor that the JOURNAL OF CHEMICAL EDUCATION was among them. Readers familiar with the delightful yet incisive prose of the many Kobe book reviews can well imagine what the support of such a contributor meant to an editor. Wise advice, based on the same clear grasp of essentials was always freely given when a referee's opinion was needed. It is a pleasure and a privilege to remember Ken Kobe.

form almost immediately. Since the reaction is an equilibrium reaction, it may take longer for some adducts to form completely. The reaction can be driven to completion by using a higher concentration of the complexing agent. For most compounds, the weight ratio of organic mixture to complexing agent to methanol of about 1:5:20 will give good results. Yields of 100% of the organic adducting are possible when the proper ratio of reactants is used.

Filtration on a Büchner funnel will separate the octanol or other non-adducting component from the adduct. Carbon tetrachloride can be recovered by decomposing the adduct by heating or dissolving in water. If water is used, the carbon tetrachloride will separate into one phase and the thiourea will be in the water phase. The table shows a list of compounds which may be used in a demonstration of the ability of urea or thiourea to separate organic compounds by adduct formation.

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(4) SCHIESSLER, R. W., AND FLITTER, D., *J. Am. Chem. Soc.*, **74**, 1720–23 (1952).
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(6) FETTERLY, L. C., *Petrol. Refiner*, **36**, No. 7, 145–52 (1957).
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Glass Rod as a Stirrer in *pH* Titrations

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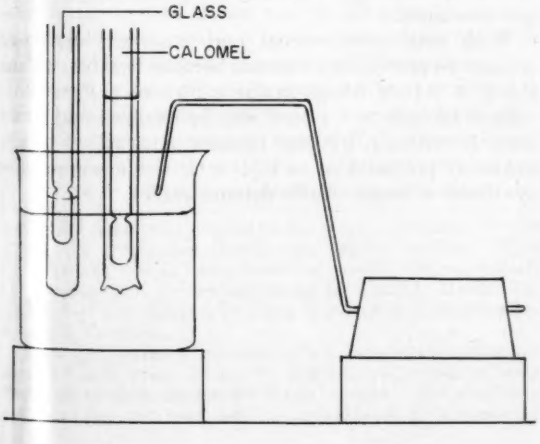
In potentiometric titrations using glass electrodes it may not be possible always to have magnetic stirrers. The use of a glass rod is attended with the inconvenience that when not in use it has to be removed from the solution or rested carefully against the wall of the beaker lest it should strike the electrode bulb and damage the electrode. A glass rod bent suitably and fixed to a cork nailed on to a wooden base, as shown in figure, obviates this difficulty. It can be manipulated by holding the base and can be left in any position in the beaker without danger to the glass electrode.



A Splashless Table Drain

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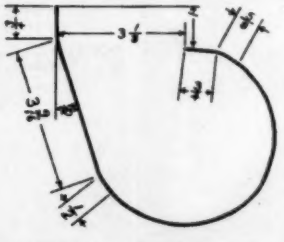
A drain that is virtually splash-free for use in a chemistry laboratory has been achieved by use of a specially shaped stainless steel trough fabricated in a local metal-working shop. The water taps are carefully aligned so that the water stream strikes a steep straight



End view of trough showing dimensions.

section of the trough. The straight section leads into a curved section that prevents any spray from escaping onto the table top. The entire trough is mounted by hooks about four inches above the table top, thereby making cleaning of the top easy.

In a test of the effectiveness of the trough in preventing spray, a water tap was run at full pressure for fifteen minutes. The total amount of spray on the table top was about 1 cc.

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A Test Tube Automatic Gas Generator

An automatic generator for producing common gases, comprising a test tube and available accessories, can easily be assembled by students for individual use. It is another modification of the Kipp (Banks, Schroeder, Starkey, etc.) generator, and was devised by the writer in 1936 to enable each person to have a simple, workable, and safe gas source. In the twenty-two years of use in freshman classes, there has been no explosion of hydrogen.

The photograph, Figure 1*A*, shows the generator in operation while 1*B* indicates the "stand-by" condition. As illustrated in the line drawing, Figure 2, one No. 4 two-hole rubber[1] stopper, holding a thistle tube and a gas effluent tube, tightly fits the mouth of a 25 × 200-mm test tube. The top half of a second similar No. 4 stopper is cut off, and the stem of the thistle tube inserted in one of the holes of the bottom piece so that this smaller stopper just slides easily into the test tube. The second holes of each stopper should be in the *cis* position relative to the thistle stem in order that the assembly may fit.

Pieces of the required solid reactant (e.g., Zn for H_2) are placed around the thistle stem on the top of the smaller stopper, and the assembly lowered into the test tube. Care must be taken to avoid dropping any zinc into the bottom of the test tube as that would make the automatic cycle inoperative.

A pinch-clamp on the rubber section of the gas delivery tube controls gas flow in the usual way. With the pinch-clamp open, the liquid reactant is poured down the thistle tube until its level is just above the solid reactant. The resultant reaction should be allowed to proceed for two minutes or so, in order to drive out air, and then the clamp should be closed. Continuing evolution of gas will increase the pressure in the generating tube, forcing the liquid surface to be lowered to a level just below the solid, with the liquid simultaneously rising in the thistle tube which thus acts as a reservoir. Opening the pinch-clamp releases gas as wanted.

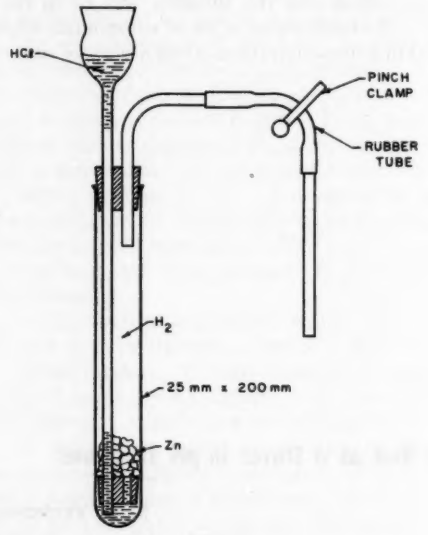

Figure 2

With such a convenient and small gas generator, semimicro process experiments become feasible. Thus, 0.5 g of copper filings in the center of a Pyrex tube (about 12 inch × 1/8 bore) can be oxidized and subsequently reduced, without transfer and with a readily achieved precision of ±1%, with the accompanying synthesis of water clearly demonstrable.

[1] Neoprene should be used when NO_2 is generated by the action of copper in nitric acid.

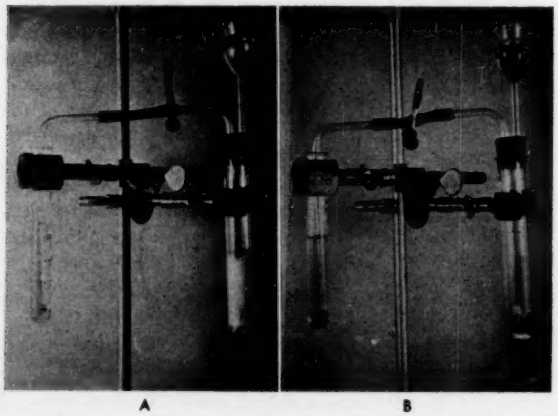

Figure 1

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Textbook Errors, 22
Miscellanea No. 3

Thermal Decomposition of Alkali Nitrates

Professor Harry Bloom of the University of Auckland, New Zealand, points out that textbooks[1] are generally in error when they discuss the effect of heat upon sodium and potassium nitrates. The statement is made that the decomposition temperature is low and that the corresponding nitrite can be thus prepared.

The behavior of sodium and potassium nitrates at atmospheric pressure has been clarified recently by Freeman (*1*). The liquids formed by melting at 307° and 334°C, respectively, undergo little change with increasing temperature until about 600°C when evolution of gas becomes appreciable and increases rapidly with temperature. Between about 600 and 700°C the principal reaction seems to be the formation of oxygen and nitrite. The reaction is reversible and under these conditions the nitrite reacts also with oxygen to form the nitrate. The reaction is slow below 600°C but reaches completion within about 2 hours at 700°. The final composition of the equilibrium liquid depends on the partial pressure of oxygen. At 1 atm pressure of oxygen an equimolar mixture of nitrate and nitrite is obtained at about 670° for the potassium salt and at about 730° for the sodium salt. At lower temperatures the proportion of nitrite decreases.

When the temperature appreciably exceeds 750–800°C in the presence of oxygen and at lower temperatures in its absence, other reactions become important, leading to formation of nitrogen and some nitrogen oxides. These are mainly due to decomposition of the nitrite with nitrogen and alkali peroxides as principal products. The latter give an orange color to the melt.

These studies were conducted in stainless steel containers which seem to have little effect upon the course of the reaction. In Pyrex (*2*) or silica (*3*) vessels the situation is much more complicated because of reaction between the molten nitrate and the silica which leads to appreciable decomposition by the time about 550°C is reached. Clay vessels cause still earlier reactions (*4*).

The end product of heating sodium nitrate or nitrite in air is obtained at about 900°C and corresponds stoichiometrically to the complete loss of N_2O_5 leaving Na_2O which is the only oxide stable at such high temperature (*5*). This result was obtained thermogravimetrically in a porcelain crucible but Dr. Freeman feels that the glaze was sufficiently inert to prevent any important side reactions in the short times involved (*6*).

Thus it appears that the sodium and potassium nitrates are quite stable thermally up to about 600°C, then decompose gradually to give an equilibrium mixture with the nitrite, and that further decomposition leading to peroxides and ultimately the oxide begins long before conversion to nitrite is substantially complete.

The Conductivity of Complexes

Professor Carlos R. Piriz Mac-Coll of Montevideo, Uruguay, points out that several texts[1] erroneously call the measured quantity used occasionally in determining the structure of complexes the "equivalent conductivity." Since the equivalent weight is unknown until the structure is determined, this may seem to be a meaningless operation. In fact, however, the quantity involved is the molar conductivity, whose calculation requires only a knowledge of the empirical formula, so that the procedure is logically consistent.

Thus Werner and Miolati (*7*) in their classical investigation of these conductivities studied two compounds of cobalt, each containing four ammonias and three chlorines. The empirical formulas were $Co(N_2H_5)Cl_3$ and $Co(NH_3)_5Cl_3H_2O$, respectively. The clearly different colors led to their common names of "purpureo" and "roseo" pentamine chlorides. The molar conductivities (i.e., the specific conductivities of their solution divided by the formal concentration) were found to be about 261 and 393 mho, respectively, at 25°C and 10^{-3} *M* concentration. By comparison with molar conductivities of other salts this can be interpreted as indicating that the former gives only three ions in solution while the latter gives four ions, so that their formulas are $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5H_2O]Cl_3$, respectively. (Historically these formulas had been established earlier on chemical grounds and the measurements were used to establish the relation between structure and conductivity.) Once these formulas have been established, the equivalent conductivities can be calculated by dividing by 2 and 3 to give 130.5 and 131, respectively.

It would seem reasonable to suggest that the distinction between molecular and equivalent conductivity be clearly distinguished by using a different symbol. μ and Λ have been frequently used in this sense. The International Union of Pure and Applied Chemistry has however deemed it advisable (*8*) to recommend Λ for "equivalent or molar conductance of electrolyte or ion." Thus the use of Λ for molecular conductivity has support but its meaning should be made very clear by the context.

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

Gram-Molecular Weight

Dr. J. R. Lakshmana Rao of the University of Mysore brings up the point that many textbooks[1] are obscure in their definition of gram quantities such as gram-molecular weight. This is sometimes given as the molecular weight expressed in grams immediately after a discussion pointing out that the molecular weight is a dimensionless ratio which clearly can be expressed only by a pure number. In fact, of course, the gram quantities are definite amounts of matter whose weight in grams is numerically equal to the corresponding dimensionless quantity.

Discussed Elsewhere

Teleology. Expressions which, when taken literally, indicate purpose and will where there is none are thoroughly analyzed by Professor A. J. Bernatowicz in a recent issue of *Science* (*9*). He presents also a number of arguments for their careful avoidance. While he covers the whole field of science, chemistry is well represented among his examples which include such common statements as "atoms strive to attain the stable arrangement of electrons that characterizes the inert gases."

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Ethyl Corporation
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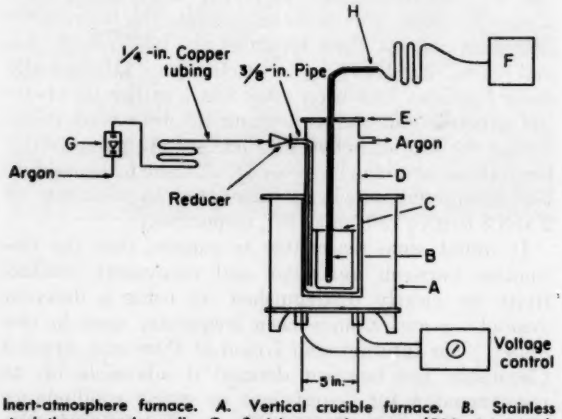
Inert-Atmosphere Furnace for Laboratory Use

Many different types of inert-atmosphere furnaces are being used today in research on titanium, zirconium, etc., several of which have been described in the literature. Most of them are rather elaborate, however, and often they are expensive to construct. The inert-atmosphere furnace described below can be constructed from standard laboratory equipment or from items which can be fabricated easily.

The basic heating unit is a standard (Hoskins) laboratory crucible furnace with a heating chamber 5 in. in diameter and 5 1/2 in. deep; the furnace operates on a standard 110-v, 60-cycle circuit and does not require special wiring. The atmosphere chamber is a piece of 4-in. mild steel pipe, 4 1/2 in. o.d., closed at one end by welding to a 4 1/2-in. diameter disc, and equipped for gas-purging by welding lengths of 3/8-in. pipe as shown in the figure. A simple slip-fit lid is made of a piece of 3/16-in. mild steel plate with a 1/2-in. diameter hole in the middle. The atmosphere chamber is connected to a cylinder of compressed argon or helium by 1/4-in. copper tubing, coiled as shown to permit flexibility in moving the chamber. The reaction chamber used for most experiments was a 500-ml stainless steel beaker, but can be a large refractory crucible or any container which will withstand the operating temperature of the furnace.



Inert-atmosphere furnace. *A.* Vertical crucible furnace. *B.* Stainless steel thermocouple well. *C.* Stainless steel reactor (500-ml beaker). *D.* Atmosphere chamber. *E.* Lid for atmosphere chamber. *F.* Potentiometer. *G.* Rotameter (flowmeter). *H.* Chromel-alumel thermocouple.

A length of 1/4-in. stainless steel tubing, closed at one end, and bent as shown in Figure 1, is inserted through the hole in the lid and serves as a combination stirrer and thermocouple well. The bent portion of the tube provides a handle for grasping the stirrer without encountering the hot zone directly over the furnace chamber. The thermocouple wire should be long enough to permit manipulation of the stirrer.

This inert-atmosphere furnace has been used quite satisfactorily for laboratory reduction of metal oxides, dehydration of salt hydrates, melting of certain metals, and other high-temperature, atmospheric-pressure operations up to about 1000°C. The coiled length of flexible copper tubing permits removal of the hot reactor for rapid cooling, if necessary, without interruption of the protective atmosphere flow.

Division of CHEMICAL EDUCATION
American Chemical Society

Suggestions for Institutes and Conferences: Summer 1960

During its meetings in Boston the Division of Chemical Education's Committee on Institutes and Conferences reviewed the summer institute programs for the summer of 1959 with an eye toward discovering how this committee might best serve to help make these programs—when viewed on a national scale—the most effective and efficient possible. As a result of these considerations the committee submits the following suggestions to those who plan to submit proposals for science teacher institutes and conferences to be held during the summer of 1960:

(1) A definite need exists for more institutes devoted to study in a single discipline as opposed to institutes devoted to study in two or more disciplines. This year 23 institutes of the 350 sponsored by the National Science Foundation are "chemistry only" institutes. Fourteen of these are for secondary school and/or junior college teachers. Six are for college teachers.

There are at least two good reasons for encouraging single subject institutes. First is the fact that most teachers feel their energies are not efficiently utilized when they have to study two or more subjects during the short summer session. Many institute directors and instructors can testify to the inefficiency of such a program. Some, however, hold to the notion that because nearly all secondary school teachers must teach at least two sciences, it is wise to try to update them in several areas simultaneously on the grounds that the teacher may not get an opportunity to return to summer school soon again. With the multiple opportunities now available for subsidized summer teacher training this notion seems untenable.

The second reason for encouraging single subject summer institutes is that these can provide better service for the participants through more homogeneous grouping. With numerous single subject institutes it should be possible, for example, to have some aimed at those who teach chemistry as their "second" subject, others designed for teachers who have been teaching chemistry for 15 or more years and still others for those who are far enough advanced to help pioneer entirely new approaches to the teaching of introductory chemistry. Homogeneous grouping, if carried to extremes, has certain drawbacks but many directors with long experience in this work feel that the advantages of homogeneous grouping far outweigh its disadvantages at this point in the development of teacher training programs.

These are the principal reasons the Committee on Institutes suggests that more proposals be submitted for institutes in which teachers study chemistry only. Proposals for summer institutes sponsored by the National Science Foundation must be in Washington by August 1.

In an effort to help stimulate proposals and assure some coordination of summer institutes, a subcommittee on summer institute activities has been established. Those wishing more information pertaining to the problem discussed here may contact the chairman of this subcommittee who is

Otto M. Smith
Kansas State Teachers College
Emporia, Kansas

(2) Because of the temendously accelerated formation and expansion of junior colleges, more institutes and conferences designed for teachers of chemistry at these institutions are needed. Here again the varied background and experience of teachers makes this an area where carefully planned institutes or conferences can make significant contributions to chemical education. Those desiring more information concerning proposals for institutes for junior college teachers may contact the chairman of the subcommittee on junior colleges who is

Robert K. Fitzgerel
Junior College of Kansas City
Kansas City, Missouri

(3) One of the newest programs of the institutes section of the National Science Foundation is the summer conference for college teachers. These conferences are designed for such purposes as consideration of specialized topics or recent advances in a particular area. They are of one to three weeks duration and are usually held either at the beginning or end of the summer so that college teachers involved in teaching summer school may participate. During the summer of 1959 six conferences in various areas of chemistry will be held. The need for more and varied conferences of this type is obvious. The subcommittee on conferences is currently stimulating proposals and soliciting suggestions for topics, possible directors, and host institutions for conferences to be held in 1960. Suggestions may be sent to

W. T. Lippincott
Department of Chemistry
University of Florida
Gainesville, Florida

or information on the preparation of proposals is available from the Institutes Section, National Science Foundation, Washington 25, D. C.

These suggestions pinpoint only a few of the areas in which institutes and conferences can serve to meet existing needs. The Committee on Institutes and Conferences invites comments and suggestions relative to improving present programs or stimulating the development of new programs.

WILLIAM B. COOK, *Chairman*
W. T. LIPPINCOTT, *Secretary*
Committee on Institutes and Conferences
Division of Chemical Education

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

Robert T. Rubin[1]
University of California
School of Medicine
San Francisco 22

Some aspects of Anti-acetylcholinestrase Chemistry

All known enzymes are themselves proteins and they catalyze certain specific chemical reactions in biological systems. They are often named on the basis of the principal substance that undergoes a reaction caused by such catalysis. Thus an enzyme that catalyzes hydrolysis of a protein is given the name of the protein substrate plus an "ase" ending, so that it is a proteinase. Similarly an enzyme that catalyzes hydrolysis of an ester could be called an esterase. One of the biologically important and well-known esters is acetylcholine, whose structural formula is

$$(CH_3)_3N^+—CH_2—CH_2—O—CO—CH_3\ ^-OH$$

The existence of a type of esterase with well-defined properties and a high specificity for acetylcholine has been firmly established (*1*), and its suggested role in the general mechanism of synaptic transmission in the nervous system of the living organism has been well documented. The enzyme is found in all mammalian nerve tissue, and the hydrolysis of acetylcholine by this enzyme has even been implicated in the propagation of the impulse along a nerve fiber (*2*, *3*).

Because certain diseases are recognized as having their origin directly within this acetylcholine-acetylcholinesterase system (e.g., myasthenia gravis) and are treated by regulating this system, the chemistry of acetylcholine hydrolysis and, in particular, of inhibitors of acetylcholinesterase is important not only to the chemist but also to those involved with practical management of diseases and clinical conditions requiring acetylcholinesterase control.

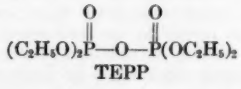
A great variety of substances have been studied in regard to their effectiveness as inhibitors of cholinesterases. One table lists over a hundred compounds (*4*). The groups of inhibitors most important from a standpoint of both their potencies and their applicabilities appear to be certain alkaloids, e.g., eserine, prostigmine, and their homologues, and the alkyl phosphates. The former class contains compounds used clinically as drugs. The latter group, the alkyl phosphates, was found during the war to be a group of extremely potent inhibitors of esterases. These alkyl phosphates are the active principle in many insecticides, and one member of this group, DFP (diisopropyl fluorophosphate), is a powerful chemical warfare agent. It was thought that in contrast to other anticholinesterase agents, the alkyl phosphates inactivate the esterases irreversibly, but recently it has been demonstrated that certain hydroxamic acids are capable of reactivating alkyl phosphate-inhibited cholinesterase (*5*, *6*). The possibility of these being antidotes for the alkyl phosphate agents of chemical warfare is currently being investigated.

[1] The author is a second-year medical student.

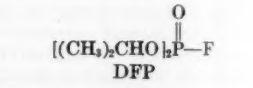
Kinetic Studies

The most illuminating approach to an understanding of the function of anticholinesterase compounds has been through a study of the kinetics of enzyme inhibition, and from these studies the mechanism of inhibition has been elucidated (*7*).

In the alkyl phosphate class, TEPP (tetraethylpyrophosphate) was found to have an almost immediately irreversible action.



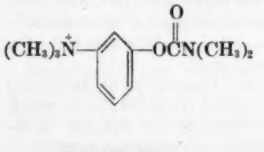
TEPP



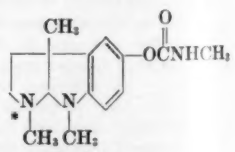
DFP

Enzyme incubation with TEPP at 10° and subsequent assay of enzymic activity shows a rapid irreversible inhibition; in contrast, incubation with DFP under the same conditions may require two to three hours for the inhibitory process to become irreversible. The effect of TEPP is not only faster than that of DFP, but it is also more potent, as shown by the fact that a lower concentration of TEPP is required for 50% inhibition of enzyme activity.

Among the alkaloids, prostigmine and eserine inhibition are both competitive and reversible.



Prostigmine



Eserine

* Acquires a proton in acid media.

When acetylcholinesterase is incubated with prostigmine before acetylchloine is added, the initial inhibitory effect is greater than if the substrate is added contemporaneously with the inhibitor, as reflected by the difference between the initial reaction velocities of the two cases. In the first case the inhibitor binds to the enzyme before the substrate, acetylcholine, is present; in the second, there is a competition between substrate and inhibitor for the enzyme. However, after equilibrium has been reached the reaction re-

lo ities for a given concentration of prostigmine and ac etylcholine are the same. This is consistent with other observations indicating that prostigmine inactivates the enzyme completely reversibly, as is also the case with eserine, which behaves similarly and has an effect about 2.6 times stronger than that of prostigmine. Eserine, however, has been shown to have been inactivated in experiments with serum cholinesterase (*8*), and such inactivation may be responsible for reduced inhibition by eserine over long periods of time.

Graphic portrayal of cholinesterase inhibition as a function of inhibitor concentration yields a straight line, indicating that these two alkaloids inhibit enzyme activity by reacting reversibly at the same active center as does acetylcholine. This is also reflected in the competitive inhibition between acetylcholine and these inhibitors.

In the case of the so-called irreversible inhibitors, the alkyl phosphates, inhibition is independent of substrate concentration; however, if acetylcholine is added before the inhibitors, much higher concentrations of the latter are required to obtain the same degree of inhibition achieved after incubation of the enzyme with inhibitor alone. That these irreversible inhibitors, as well as the reversible ones, act on the site of attachment of acetylcholine to the enzyme molecule was suggested by this protective effect. This is substantiated by protective effects exhibited by prostigmine against enzyme inactivation by DFP (*7*).

Mechanism of Action

Because the normal substrate and many inhibitors are positively charged, the idea is tenable that there is a negatively charged region within the enzyme, properly shaped and spaced, which enhances enzyme activity by helping to fix the substrate to the enzyme surface (*9*). Indeed it was shown that the rate of hydrolysis of dimethylaminoacetate is about three times more rapid in acidic solution when this substrate exists as the cation, than when it exists as the uncharged molecule in basic solution (*10*). The change in enzyme activity as a function of *p*H was studied with acetylcholine as the substrate since this molecule does not alter its charge with change in *p*H (*11*). This activity factor has been taken into account in the ratio quoted above for the dimethylaminoacetate studies.

Further evidence for the existence of the anionic site on acetylcholinesterase is to be found in studies with eserine and prostigmine (*10*). Prostigmine, a quaternary ammonium cation, was shown to have the same inhibitory efficacy over a *p*H range of 6 to 10. Eserine on the other hand at *p*H 10, where it exists predominantly in the uncharged form, has an inhibitory effect of 20%; whereas at *p*H 6, where it is principally in the cationic form, eserine produces 80% inhibition. (Refer to the chemical formulas.) Thus ionic bond formation binds the cationic substrate or inhibitor to the anionic site on the enzyme. Van der Waals forces are active in the binding of both charged and uncharged molecules to the enzyme.

The existence of an "esteratic" site has also been amply confirmed. This site contains a basic and an acidic group, both necessary for enzymatic activity. During hydrolysis the esteratic site makes a combined acid-base attack upon ester substrates, and the basic group becomes acylated. The acyl enzyme thus produced reacts with water to yield a carboxylic acid and the free enzyme (*9*). For example, the reaction between an alkyl phosphate, here a fluorophosphate, and a cholinesterase, has been described as

$$\text{H—}\ddot{\text{G}}\text{:} + (\text{RO})_2\overset{\overset{\text{O}}{\|}}{\text{P}}\text{—F} \rightarrow \text{G—}\overset{\overset{\text{O}}{\|}}{\text{P}}(\text{OR})_2 + \text{HF}$$

H—G represents the esteratic site of the enzyme, with H being the acidic group and G the basic group with its electron pair, where bond formation with the alkyl phosphate occurs. In this phosphorylated state the enzyme-phosphate bond is not readily hydrolyzed, as is the acetyl bond in the complex formed with acetylcholine. Thus the active enzyme is not quickly reformed, and effective inhibition is the result.

As noted previously, certain compounds, particularly hydroxamic acids, were recently shown to be capable of effecting the reactivation of cholinesterases inhibited by alkyl phosphates. These compounds can form complexes with TEPP-inhibited enzyme similar to active enzyme-substrate complexes, since the anionic site escapes being affected by the alkyl phosphate. Gaining attachment to the anionic site, they can then combine with the phosphoryl portion of the inhibited enzyme, thereby freeing the active enzyme (*12*).

A third class of anticholinesterase agents has been used to investigate the fine structure of the enzyme surface (*13*). These compounds are reversible, competitive inhibitors, and have two essential structural features. A polymethylated, sometimes quaternary nitrogen atom serves as the point of attachment to the anionic site of the enzyme. Separated by approximately the distance of a $—CH_2CH_2—$ unit from the ammonium group is a simple high electron density group, a ring nitrogen atom. An example is N(*β* dimethyl aminoethyl) piperidine. This arrangement suffices to complete the binding process by fulfilling the steric and electrostatic requirements of the esteratic site, thus providing extremely effective enzyme inhibition. By varying the distance between the two groups and correlating this with inhibitory efficacy, the steric relationship between the anionic and esteratic sites may be determined.

In summary, several types of anti-acetylcholinesterase compounds have been discussed, and their practical applicabilities have been alluded to. The alkaloids prostigmine and eserine are reversible, competitive inhibitors. The alkyl phosphates, such as DFP and TEPP, have been shown to have an almost irreversible action, and to act at the same site on the enzyme as do prostigmine and eserine, which site is indeed the active center for acetylcholine. These conclusions were based upon evidence of protective effects of acetylcholine or of one inhibitor against another. Finally, the investigation of the fine structure of the enzyme surface has been conducted, using a third group of anti-cholinesterase agents.

Although much has been learned about the properties of acetylcholinesterase from the action of many different types of inhibitors, the characterization of this enzyme is not complete. The localization of acetylcholinesterase in nerve tissue remains to be definitely

established, and a fuller description of its physical and chemical properties awaits the crystallization of this enzyme.

Acknowledgment

The author wishes to thank Mr. R. C. Fay for many helpful suggestions.

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Chem Ed

LETTERS

To the Editor:

The February article on the "Explosive Hazard of Aluminum-Liquid Oxygen Mixtures" by Austin, *et al.*, certainly was timely. It serves to point up the fact that aluminum powder—and perhaps other metal powders—may not be the innocent materials they seem to be. The following experience illustrates this.

About 10 years ago I was engaged in preparing suspensions of aluminum powder (aluminum "bronze") in technical-grade oleic acid. One such mixture, 20% aluminum powder (w/v), was made up to fill a small glass bottle (50 ml). After the powder was added to the oleic acid and the mixture gently shaken, I set the bottle on the lab bench and walked into the other room. The bottle was left unstoppered.

In approximately 3 to 5 minutes a low-order detonation occurred, completely shattering the bottle and throwing fragments of glass as far as 15 feet away. A substantial rise in temperature was not detected, nor was there a flash.

I have tried, quite unsuccessfully, to repeat this effect since then, using the same batches of aluminum powder and oleic acid as originally employed.

The force of the curious explosion was such that a person standing near the bottle could have been blinded by flying glass particles.

JACK DE MENT

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5919 SOUTHEAST 72ND AVENUE
PORTLAND 6, OREGON

To the Editor:

In the first paragraph of the recent article by Austin, Rohrer, and Seifert, entitled "Explosive Hazard of Aluminum-Liquid Oxygen Mixtures" (J. CHEM. EDUC., **36**, 54 (1959)), the authors refer to the original description by Cady (*Ibid.*, **8**, 1027 (1931)) of a lecture demonstration consisting of the ignition of such a mixture. I should like to point out that the conditions which are described as having been used in most of the trials at the Naval Ammunition Depot differed materially from those described by Cady in the 1931 article. Thus, it is stated in the recent article that "the general procedure was to place aluminum powder in an iron crucible contained in a larger iron dish *half full of sand.*"[1] This practice may very well have been based upon a misunderstanding of Cady's use of the term "iron sand-bath." In Cady's article, the reference to the preceding experiment (Experiment 19, page 1039) clearly shows that this term was used merely to designate the dish itself; there is no mention whatever of the use of sand. Furthermore, in most of the trials at the Naval Ammunition Depot, the aluminum was contained in a crucible of such dimensions that the upper surface of the powder was only *1.5 inches (3.8 cm) in diameter.*[1] Cady, on the other hand, recommended the use of an iron dish 12 cm in diameter. Obviously, even if 50 ml of powdered aluminum were used in such a dish the layer would not be more than 5 mm in depth. It is evident, therefore, that most of the N.A.D. tests were made under conditions much less favorable to the rapid dissipation of heat than those described in Cady's article.

[1] Italics mine.

ARTHUR W. DAVIDSON

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

(*Letters continued on page 310*)

Report of the New England Association of Chemistry Teachers

David G. Barry[1]
Mankato State College
Mankato, Minnesota

Science Fairs in Perspective

With the arrival of spring, come the Science Fairs in the schools of the nation. Current stress on education in the sciences will cause these events to increase in number and in influence. This can be a good trend but, like all things in education, the effect on the shaping of young minds depends on the goals and the standards that underlie the planning. Because these events have such potential for development of future scientists, I believe that it is imperative for all men of science to become more aware of their existence and their problems.

Wolfle[2] has suggested that society is having difficulty digesting ideas of the power and magnitude of the bombs of the atomic era. He offers this as a symptom of the fact that science gains continually in its power to modify our environment and thus poses problems that are of increasing urgency to society. It is his opinion that "as scientists gain greater and greater understanding and control of the forces of nature, it becomes of mounting importance for society to make the right decisions concerning the support of science and the control and utilization of Scientific Development." In chorus with him we all speak for more effective education in the sciences. Science Fairs are one of the many activities which can further this goal and which deserve support of all men in science. The teachers who are organizing these events should not be left to stand alone. They need our support and cooperation in accomplishment of our common goal.

For the parent and the public, the Science Fair is another opportunity to see science in operation. It is an opportunity for scientists in the schools to attract the interest of the public, to recruit their support, and to contribute to their understanding of the nature of scientific thought and inquiry as a fundamental philosophic outlook on the world. These Fairs can serve as a tool of science both in the encouragement of future scientists and in the education of the general public. However, without recognition of some of the problems, there is a possibility that in some instances student participants will be frustrated, will have their interests blunted, and an already confused view of science will be furthered in the public mind.

The promotional uses to which the name science is given by what Galbraith calls our "Affluent Society," offers a definition of science which poses a certainty and arrogant sureness that is false. The scholar in science knows well that no other human endeavor is as filled with doubt and uncertainty as modern science. The mechanical certainties of the eighteenth and nineteenth century science are no longer with us. Men who work in science reach a point after which they feel partially sure of their results, sure enough to act on them but never at the level of certainty offered to the public by the pseudo-scientific salesmen who shout out from our mass communications systems. It is no small wonder that people are confused concerning the nature of science. Perhaps men can never see very clearly the forces that shape their personal lives, but we must try. Too many people in and out of science mistake the products of science for the intellectual endeavor itself. Thus we depend on these products for a view of science and do not develop an adequate comprehension for the development of the ideas in the minds of men that have made these products possible. This is a confusion of the worst order because it allows society to move into the twentieth century period of "power science" with views that attribute the certainty of magic to science. We confront a world that can be partially measured, can be manipulated within limits, and that seems to be constructed of series of most probable but uncertain events. Today, with atomic energy in our hands, we live within limits of peril which make it imperative that we lead in every possible way to make science, as a philosophic effort, be understood.

Emphasize Understanding; De-emphasize Gadgetry

In the ideal Fair, it is to be hoped that the project a student selects for development will give him opportunity to demonstrate his level of understanding in the area of study that is of personal interest to him. He is urged to be independent, personally imaginative, and as creative as possible in his work. It is desirable for the student to gain an appreciation of what constitutes a scientific principle; not just to handle some of the materials of science but to experience science as an intellectual, creative activity; to become aware of the difficulty of doing something that is new or of developing techniques that will test and demonstrate an hypothesis be it old or new. Such experiences can give a student insight into the intellectual honesty he must develop to think and act as a scientist. Perhaps the greatest social result is the discovery of our most fundamental natural resource—the young men and women that have poten-

[1] NSF Faculty Fellow, Harvard University, 1958–59.
[2] Wolfle, Dael, *Science*, **125**, 180 (1957).

tial for the leadership human society requires for continued existence in a world of change.

The teacher who directs the student's project can become a problem by "entering the competition himself." If the teacher contributes too much to insure the success of the project with his own reputation in mind, the project may be a contest winner but it will be a personal loser for the student. The gain for the student lies in the experience of working as an individual, in being dependent on his own intellectual resources.

Overemphasis on technological craft and display techniques in projects can mask the intellectual character of science. It is ideas and concepts that give technique and pattern to science and not the reverse. Technology and applied science are the result of research in ideas which only later found practical application. Students should be urged toward the view that the first goal of science is the isolation and understanding of natural phenomena. Emphasis on the technical tricks of science may fool the judge but it will lead toward the confusion of science with gadgetry and magic.

The wisdom of cash prizes is questionable. This is an age of cash prizes. There are many reasons not to equate success in science with mere commercial gain. Success in science depends on intellectual growth and scholarship and should receive an award that carries prestige and appropriate recognition. It would be useful and proper to make awards that will lead the student onward in his personal development. Scholarships, books, subscriptions to science publications are but a few examples of many possibilities.

Money for Fairs is a problem. If a cash budget exists, it is usually the result of much footwork by the staff and of contributions from philanthropic individuals in the community. Investment in these fairs is an investment in science and should not be left to philanthrophy. These events should be a part of the school budget to insure their successful management and to secure competence in judging. Lunik, traveling in outer space, is disturbing evidence of the support basic science receives elsewhere in the world.

The most critical aspect of the Fair is the role of the judge. It is through the judge and his comments that the student will learn to what degree he has succeeded as a junior scientist. If the competency of the judge is in doubt, the Fair can have a negative effect. Judges should not be selected to further good public relations. They should be selected for having actually demonstrated competence as creative scientists. They should receive financial compensation for their work. Their function is critical to the future of science and well worthy of investment. Non-scientists should not be used as judges. Daily use of the products of science does not bestow competence for judging creative scientific work.

While the ideal situation described here will be reached in different degrees in different situations, it is possible for all persons in science to take more interest in and give more support to these activities which can foster the growth and development of future leaders. The benefits derived from these events will be of value if they are organized with goals and standards which represent science to the student and to the public—for what it is: an attempt on the part of man to gain dependable information and understanding about the universe in which we live; a dedication toward development of policies of behavior that will provide what we consider to be a better life for the individual and his society.

Chem Ed

LETTERS

To the Editor:

In the article of John Howe Scott, "The Nineteenth Century Atom Undivided or Indivisible?" in the February issue of the JOURNAL OF CHEMICAL EDUCATION, we read: "Lothar Meyer, who divided the Nobel Prize for the periodic table with Mendeleev." I am sorry to inform you that neither Lothar Meyer nor Mendeleev obtained a Nobel Prize. L. Meyer died in 1895 and the Nobel Prizes were first awarded in 1901.

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EDITOR'S NOTE: Our correspondent, Dr. Sementsov, has kindly pointed out an error which must have caused many a condescending chuckle among our readers. The honor shared by the illustrious founders of our modern classification scheme was the Davy Medal awarded in 1882.

To the Editor:

In answer to your query on page 170 of the April, 1959, issue of the JOURNAL OF CHEMICAL EDUCATION concerning commemorative coins in honor of scientists, I note the article entitled "A Humanist Looks at Max Planck" by James C. O'Flaherty, which appeared in *American Scientist*, **47**, No. 1, March, 1959, pp. 68-79. The following statement appears on page 78:

> It is one of the subtler ironies of history that, twenty-five years after Planck's painful encounter with the head of the German state, the Federal Republic of Germany should place the state's highest seal of approval on Max Planck, the man and the scientist, by having struck in his honor a coin bearing his likeness ....

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Chem Ed

BOOK REVIEWS

Advanced Analytical Chemistry

Louis Meites, Polytechnic Institute of Brooklyn and *Henry C. Thomas*, University of North Carolina. McGraw-Hill Book Co., Inc., New York, 1958. xi + 540 pp. 16 × 23.5 cm. $8.90.

Since this textbook does not pretend to treat the whole field of analytical chemistry, perhaps a more apt title for it would have been "Some Physico-Chemical Analytical Techniques." The treatment covers electroanalytical methods (potentiometry, conductimetry, polarography, amperometric titrations, electrogravimetry, and coulometric analytical methods), spectrophotometry, radiochemical methods, ion-exchange, and chromatography (except gas chromatography). I agree heartily with the authors' point of view that an attempt to cover the entire field of "instrumental analysis" in a book intended for a one semester course is impractical, unless one is content with superficiality. The authors decided wisely when they restricted the coverage to topics that they could discuss thoroughly with a competence rooted in their own experience.

In keeping with its intended use as a text the emphasis is on cardinal principles rather than specific analytical methods. The treatment, especially in the chapters on electroanalytical methods, is patterned closely on existing monographs but is enlivened by original examples. The discussions are critical and thoroughgoing, particularly in respect to the interpretation of experimental data. Although flavored somewhat with pedanticism the text reads well, and reflects the authors' first hand experience in teaching. Problems (answers in the Appendix) are provided in abundance at the ends of most of the chapters, and they have been selected most thoughtfully.

The last 115 pages, on Practical Applications of Instrumental Techniques, is a compilation of detailed directions for laboratory experiments. These appear to be well conceived and they are presented with exceptional lucidity. These experiments are designed to compare the various instrumental techniques in obtaining physicochemical data on a particular system (e.g., solubility of lead iodide by various methods), rather than to exemplify their routine analytical applications. The student is thus introduced to the important matter of selecting the best techniques for the evaluation of a particular thermodynamic datum. In this connection the discussion in Chap. 12 on The Development of an Analytical Method deserves high commendation.

In only a few places have I noticed imperfections. The discussion of conventions pertaining to galvanic cells on pages 18 and 19 is disappointing. On page 26, in reference to the standard potential of the stannic-stannous couple versus its formal potential in hydrochloric acid media, the assertion "Undoubtedly any attempt to use the reported values of this standard potential to describe the action of stannous chloride solutions as reducing agents could only lead to error and confusion" is unwarranted. Actually the formal potential of this couple in hydrochloric acid solutions does not differ much from its standard potential. Better examples of the distinction between standard and formal potentials could have been cited. On page 12 the effect of ionic strength on the formal potential of the ferri-ferrocyanide couple is given as the reason why ferricyanide ion oxidizes iodide ion in acid medium, but the more important effect of *p*H is not mentioned. It is unfortunate that the authors have chosen (p. 61) to use the term "differential titration" for the titration of mixtures, rather than in its accepted meaning. The statement on page 224 that conductometric end-point detection has not been applied to coulometric titrations is incorrect, since it was so employed by R. Gaugin in 1954. It is not true, as stated on page 225, that when amperometric endpoint detection is used in coulometric titrations the indicator electrode usually is a rotated platinum electrode. Two-electrode amperometry has been used much more than single electrode amperometry in this field.

Accurate assessment of a textbook can only be obtained by actual classroom use, and a review such as this can do little more than indicate whether or not a book is worthy of trial. In the present case the answer certainly is affirmative.

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Gas Chromatography

Edited by *Vincent J. Coates, Henry J. Noebels,* and *Irving S. Fagerson*. Academic Press, Inc., New York, 1958. xii + 323 pp. Many figs. 16 × 23.5 cm. $10.

This book follows a trend that is becoming increasingly evident in the publication of scientific books. A meeting is held at which a number of authorities are invited to speak on a given subject. A compilation of these papers forms the basis of the new book. In this case, a summary of the proceedings of an international symposium on gas chromatography held during August, 1957, at Michigan State University is presented. Another book, "Vapour Phase Chromatography" by D. H. Desty and C. L. A. Harbourn, editors, Academic Press, New York, 1957, describes a similar symposium held in London in 1956.

There are some advantages and many disadvantages which may be cited for this technique of book writing. It is certainly worthwhile to have the thinking and experimental results of research men working in a new field of endeavor collected in one place. This is particularly true with a rapidly expanding subject such as gas chromatography. On the other hand, this type of book will soon become outdated as theoretical and technical advances continue to be made. In fact, a considerable amount of material presented in this volume elaborates upon or replaces work reported in the earlier

Reviewed in this Issue

Louis Meites and *Henry C. Thomas*, Advanced Analytical Chemistry

Vincent J. Coates, Henry J. Noebels, and *Irving S. Fagerson*, Editors, Gas Chromatography

Thomas F. Magner, Manual of Scientific Russian

Soviet Research in Crystallography. Volumes 1 and 2

A. V. Shubnikov and *N. N. Sheftal*, Editors, Growth of Crystals

David Kritchevsky, Cholesterol

Georg Edmund Dann, Martin Heinrich Klaproth 1743–1817

Bern Dibner, Agricola on Metals

Eugene Müller, Editor, Methoden der Organischen Chemie. Band 11, Teil 2. Stickstoffverbindungen II–III

George L. Clark, Gessner G. Hawley and *William A. Hamor*, Editors, The Encyclopedia of Chemistry (Supplement)

Bruno Jirgensons, Organic Colloids

book edited by Desty and Harbourn. Because this book is not a complete coverage of present knowledge of the subject, other references must be consulted in order to understand many of the theoretical topics.

The 27 papers included in the book vary considerably in quality and content. No strict arrangement of material has been followed. The papers cover theoretical developments (7), new instrumental equipment (9), and analytical applications of gas chromatography including analysis of process streams (10). One chapter contains a discussion of the past, present, and future of gas chromatography by one of the discoverers of the method, A. J. P. Martin. A brief summary of discussion following twelve of the papers has been included. Most of the chapters contain a short list of references. In addition, a very fine annotated bibliography (487 references) is presented near the end of the book. Recent recommendations on gas chromatography nomenclature appear in Appendix I.

Of particular interest to the reviewer are the chapters dealing with gas-liquid partition chromatography in capillaries, operation of high temperature gas chromatographic equipment, a study of thermistors as katharometers, use of a combustion tube and analysis of products, apparatus for preparative scale vapor chromatography, and the continuous gas chromatographic column. For the most part, the papers are well written and carefully edited.

If extrapolation of a line through two points is justified, we may anticipate future editions of this type following other symposia on gas chromatography. Aside from the objections raised earlier, this book will be extremely valuable to anyone engaged in fundamental or applied research involving this important analytical technique.

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Manual of Scientific Russian

Thomas F. Magner, Department of Slavic and Oriental Languages, University of Minnesota. Burgess Publishing Co., Minneapolis, Minn., 1958. iii + 101 pp. 21 × 27 cm. Unbound, $4. Spiralbound, $4.60.

The stark lack of American scientists who can read the Soviet scientific literature coupled with events in the news has focused attention on the serious linguistic gap which exists in our present-day scientific environment. It is not surprising, therefore, that textbooks should appear in an attempt to close or at least narrow this intellectual breach. The "Manual of Scientific Russian" is such a book.

The author is to be commended for his teaching intent. He rightly states, in the introduction, that since the scientist who wishes to study Russian. . ."is a mature person, used to complex structures, the writer has dispensed with the slow, shock-avoiding approach of the multipurpose textbook." It is one thing to avoid shocks, and another to avoid essentials, however. For in his desire to abbreviate the study of the Russian language apropos to the time limitations and needs of the American scientist, the author has swung to the other extreme and has introduced a brevity and typographical layout which defeat his purpose. The book is supposed to serve as a combination reference and textbook. The former function is quite well served by the presentation of several useful compilations and tables. It is as a textbook, however, particularly one for self-study, that the manual has shortcomings.

The first section (pp. 3–35) which deals with the Cyrillic alphabet and Russian grammar contains the following three chief faults: (1) Deviation from the traditional order of noun declension. While the presentation is self-consistent, the student will be confused when he consults, as he must, another Russian textbook with the customary order of noun cases. (2) Indefinite typographical layout without any major chapter breaks. (3) The lack of accent marks. The student should get a "vocal feel" for Russian sounds. Incidentally, Dover Publications Inc. also retails a Russian language record for approximately one dollar.

The second section (pp. 36–49) contains paradigms (examples of noun, pronoun, and adjective declentions and verb conjugations). The grammatical formation of the verbal participles, which occur so frequently in scientific and technical Russian, are not included either in the pp. 32–33 discussion or the listing on pp. 48–49.

Reference, the third section (pp. 50–64), although attempting to simplify and categorize the irregularities of Russian nouns, adjectives, and verbs, introduces a symbolism which serves to only complicate an already complex language.

Vocabulary help is the fourth section (pp. 65–75). It contains useful discussions of word derivations, prepositions, connectives, frequently used terms, a list of the chemical elements, and available dictionaries, both general and specific.

The fifth section (pp. 76–77) which deals with the Techniques of Translation approaches the translating process from the grammar point of view.

The sixth, and last section (pp. 78–100) is concerned with excerpts from Russian scientific texts and journals for reading practice and the last portion consists of a glossary.

The reviewer sympathizes with the author in his desire to approach the study of the Russian language used in scientific texts, without having to resort to reading Pushkin's poetry. There is a minimum aspect of the Russian language, however, which the conciseness of this book with its lack of exercises, examples of sentences, etc., does not completely fulfill. In conjunction with a standard Russian grammar, however, this manual is certainly a step in the right direction.

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Soviet Research in Crystallography. Chemistry Collection No. 5. Volumes 1 and 2.

Consultants Bureau, Inc., New York, 1958. Vol. 1, 388 + vi pp. Vol. 2, 229 + vi pp. Many figs and tables. 21.5 × 27.5 cm. Paper bound. Vol. 1, $100. Vol. 2, $30. The set, $115.

Growth of Crystals

A. V. Shubnikov, Academician and *N. N. Sheftal*, Editors-in-Chief. Consultants Bureau, Inc., New York, 1958. 294 pp. Many figs. 21.5 × 27.5 cm. Paper bound. $15.

These three volumes are translations by the Consultants Bureau, Inc., of reports on Russian research.

That on growth of crystals covers a conference held in March of 1956. The papers are divided into those which deal with: (1) general questions, (2) theory, (3) experimental research, (4) growing of crystals, apparatus, and method, (5) miscellaneous. Most of the currently active fields are discussed and the general content of the papers is at a high level.

The two volumes on crystallography cover a total of 185 papers. The majority of these are concerned with X-ray studies of multicomponent systems, but there is some work on structural studies, theory of structure, analytical, and more general topics.

All three volumes suffer at times from translational difficulties, but these never seem to be serious enough to be really confusing. An ancillary observation from perusal of the three volumes is the large degree to which the Russians cite primarily their own literature. I was personally discouraged to find this American fault occurring in these papers.

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Cholesterol

David Kritchevsky, Associate Member, the Wistar Institute, Assistant Professor of Biochemistry in Medicine, The University of Pennsylvania. John Wiley & Sons, Inc., New York, 1958. xi + 291 pp. 15.5 × 23.5 cm. $9.75.

Considering the many facets which the work on and with cholesterol has assumed in the last half century, the writing of a book on this substance appears as a singularly bold undertaking. The useful organization of the unending amount of literature on cholesterol is a tremendous task for a single scientist, and for this reason the enterprise which Dr. Kritchevsky has shown in making his compilation would still call for our admiration, even if he had not succeeded as well as he did.

The first chapter of this book gives an adequate review of the chemistry of cholesterol and the elucidation of its constitution. The more recent work on the total syntheses of this substance is described in sufficient detail and a special place is given to the syntheses of the

(Continued on page A368)